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DIRECT DETERMINATION OF METALS IN AIR

Louisiana State University

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ABSTRACT

An instrument has been developed capable of the direct determination of metals in air. No prior scrubbing or extracting of the metals from the air is necessary. Consequently, the time necessary for analysis is a matter of minutes - permitting real time analysis to be carried out on small volumes of air.

The method was based on atomic absorption spectroscopy and involved the development of a highly efficient atomizer. The sensitivity of the method was determined to be about 10^{-12} g. Procedures for the direct quantitative determination of lead, mercury or cadmium in the air were developed.

Problems were encountered with traces of impurities in the system. Normal 'trace' levels are unacceptable at the levels necessary for direct metal determination. Calibration techniques were especially difficult to develop and numerous methods were studied. The calibration methods which were found to be useful at these concentrations were developed into reliable analytical techniques. These methods are described.

Preliminary studies indicated that other elements such as Ag, K, Na, Se, As, Cu, and Zn were also detectable in air; but calibration techniques for these methods have not yet been developed.

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SECTION I

CONCLUSIONS

1. A research instrument capable of the determination of metals in the 10^{-12} g level has been developed.

2. The instrument has been shown to be capable of the detection and determination of Pb, Cd, Hg in the air in real time.

3. Other elements such as Na, K, Cu, Zn, As, Se have been detected in air, but calibration techniques must be developed to obtain quantitative data for the results.

4. Impurities in the reagents used pose a major problem at these levels. So far it has only been possible to remove them in the equipment itself.

5. Calibration techniques at this level presented a problem, but successful methods have been developed.

6. Further experimental work is necessary to extend the technique to less volatile metals.

SECTION II

RECOMMENDATIONS

Based on the results it appears that the more volatile elements such as lead, mercury, cadmium, etc., can be determined directly in the atmosphere. The results also indicate that a higher temperature furnace would permit the detection and determination of many other less volatile elements.

It is recommended that such a high temperature furnace be designed and tested for quantitative determination of the less volatile pollutants in the atmosphere.

The second recommendation is that a miniaturized instrument be developed capable of being transported from one location to another to allow direct analysis of the atmosphere at various sites.

These sites would include suspected sources of pollution. The sensitive areas which may be exposed to high pollution or in which it is important to know the pollution exposure level, such as school yards, streets, factory workshops, inside homes, inside transport vehicles such as airplanes, motor cars, etc., and remote areas where it is suspected that pollution levels should be very low, could be easily measured with the miniaturized equipment.

SECTION III

INTRODUCTION

Scope. The scope of the work was to develop an instrument capable of ultra sensitive determination of metals.

Purpose. The purpose was to provide an instrument capable of real time analysis of individual metals in the atmosphere, these metals would include these obtained in particulates and those in molecular form.

Such a device would permit the observation of the concentrations in air of dangerous metals such as lead, mercury, cadmium, arsenic, silver, etc. Based on this information warning systems and control mechanisms could be created.

It was also intended to carry out preliminary work on the development of a field method based on this technique. Such a field instrument would be portable and capable of locating sources of pollutants. In addition, it would provide the capability of running analyses of air which is normally inaccessible to conventional equipment such as on top of buildings, in machinery or in rural areas.

Background. The current methods for the determination of metals in the atmosphere generally follow the procedure (a) scrub a known volume of air over an efficient scrubbing agent, (b) analysis of all or part of the scrubbing solution after extraction of the metal from the atmosphere, (c) based on this analysis the concentration of metal in the original air volume can be calculated.

This procedure suffers from several rather important disadvantages. First, it is invariably not possible to carry out real time analyses. The sample collection and subsequent analysis of the scrubbing mixture always takes a finite time. In the case of some metals such as mercury, this time is relatively short, but in the case of other metals the time lapse may be several hours or even as long as a full day. Such long times prevent the techniques from being used as the basis of control systems and at best only provide data on average concentrations during that time period. The principal usefulness of such data is the long term evaluation of various inputs into the atmospheres. This is a valuable contribution but does not get to the heart of pollution control.

Second, the use of scrubbing solutions in analytical procedures always leaves open to question the efficiency of the scrubbing mixture. Any particular scrubbing mixture is rarely a 100% efficient even when used under the correct operating conditions. If the operating conditions are less than optimum the scrubbing efficiency decreases and the analytical error is increased.

In addition, the scrubbing mixture itself may include as an impurity the metal which is being determined. Although it is quite often possible to correct for this source of error there is always the distinct likelihood that the correction will not be made or that an inaccurate correction will be made. In either event the analytical data obtained may be inaccurate.

It can be seen quite clearly that scrubbing techniques can easily lead to inaccurate analytical data. However, it should be pointed out that the reason that scrubbing techniques have been used is because of the very low concentrations of metals generally encountered in polluted air. For example, it is common for the concentration of lead to be about one microgram per cubic meter of air. This means that if one cubic meter of air were scrubbed and all the lead extracted, then one microgram of lead would be extracted and must now be determined. This in itself is quite a feat and challenges the sensitivity of most conventional analytical techniques. It can readily be understood that impurities in the solvent or any inefficiency in scrubbing can lead to a major percentage error in the final determination. For this reason it is frequently necessary to scrub several cubic meters of air in order to get sufficient metal to complete an analysis. This takes time and leads to the problems of real time analysis referred to earlier. It was our belief that approximately 50-100 cc of air could be viewed at any one time and that determination of the metal in that quantity of air would necessarily require high sensitivity, i.e., in the order of 10^{-10} g. At the time of inception of this research proposal no such analytical techniques were available, but it was felt that the advantages of such methods justified the research effort.

Theoretical Approach. It was decided to devote our primary attention to the development of a technique based on atomic absorption spectroscopy. The reasoning behind this decision was that it had already been shown that atomic absorption spectroscopy was capable of reaching sensitivity limits in the order of 10^{-7} g and in the case of a few elements 10^{-8} g. Thus, it was felt that the method was already capable of high sensitivity, although not sufficiently high for direct determination of metals in air but within striking distance.

Secondly, there is ample evidence in the literature that atomic absorption spectroscopy enjoys a high degree of freedom from analytical interferences and is therefore more accurate than most other analytical techniques. The method is based on absorption of radiant energy by free atoms. The degree of absorption is a function of the number of free, unexcited atoms in the system and therefore to their concentration. Thus, within the first approximation it is independent of the temperature of the system. Secondly, since many metal compounds are decomposed in flames or other atomizers, the percentage of atoms reduced to free atoms is fairly constant and independent of the chemical form. Unfortunately, there are numerous exceptions to this generalization particularly where the metal forms very stable compounds with the flame products. There is a proportional decrease of atom population and

consequently a lap in absorption signal for a given sample concentration. This gives rise to chemical interference. It is one of the major problems of the technique. It would be necessary to develop a procedure which was independent of the chemical form of the metal. The analytical signal from any one metal such as lead in the atmosphere would not depend on whether the lead existed as tetraethyl lead, lead bromide, or lead oxide or any other lead compound. It was felt that atomic absorption spectroscopy could be capable of providing the basis for such a procedure.

The proposed technique, therefore, has two very strong points of recommendation: (1) high sensitivity and (2) a high degree of freedom from interference effects and therefore a high analytical accuracy.

Factors Controlling Sensitivity. The mathematical relationship relating the degree of absorption and the number of atoms in the light path is given by

$$\int_0^\infty K_\nu d\nu = \frac{\pi e^2}{mc} Nf$$

Where $\int_0^\infty K_\nu d\nu$ equals the total amount of light absorbed at frequency ν, $\frac{\pi e^2}{mc}$ have the conventional meanings, c is speed of light, e is change of the electron, N is the number of atoms in the light path and f is the oscillator strength of the energy transition involved in the absorption.

Generally, it can be assumed that function of the atomizer is to charge the sample element from an ionic form or an organometallic form to a free atomic form, i.e., sample $\xrightarrow{\text{atomizer}}$ free atoms N.

The efficiency of producing free atoms from the sample is controlled entirely by the atomizer used. At the time that this work was initiated, the standard atomizer system used in atomic absorption spectroscopy was the flame. Sensitivities in the region of 10^{-6} to 10^{-8} were common using flame atomizers.

If time is taken to envision the situation of a free atom liberated in a flame atomizer it can be readily noted that the free atom is in an extremely hot plasma surrounded by very reactive chemicals. It is not surprising, therefore, that the free atoms rapidly combine with some other chemicals present in the flame and form a compound such as an oxide or hydroxide, etc. When that happens the atom is removed from the free atomic population. The latter is, therefore, rapidly lost.

Earlier calculations have shown that approximately 1 atom in 10^8 is actually reduced to the free atomic state in the flame.[1] It was felt that the atomizer is a very weak link in the process used in atomic absorption spectroscopy.

Early work by L'vov[2] had shown that a carbon tube could be used as an atomization system and that high sensitivities in the order of 10^{-11} g were achievable. However, all his work indicated that quantitative analyses were extremely difficult because of the poor reducibility of the system.

L'vov's work was neglected for many years, but it was felt that it could serve as the basis for a quantitative method of analysis.

The approach taken in this work was to use an atomizer composed of heated carbon in which atomization took place, the free atoms then issuing into an absorption tube at right angles to the atomization tube as indicated in Figure 1. Indications were that separation of the atomization chamber and the absorption chamber would eliminate many of the causes of interference encountered in the L'vov process. For example, the combustion products when organic compounds were analysed would be burned in the atomization stage and reduced to carbon monoxide. This complicated procedure always produces a high background; however, with the process used, this would take place out of the absorption tube and would not be a source of interference.

Atomization Step. The atomization of the free atoms was based on the use of hot carbon over which the air sample was drawn. The air sample was composed, naturally, of nitrogen plus oxygen and the following reaction with carbon took place: $C + N_2 + O_2 \rightarrow \begin{matrix} CO + N_2 \\ \downarrow\uparrow \\ CO_2 \end{matrix}$

The carbon monoxide formed was in equilibrium with carbon dioxide and at temperatures above 900°C the equilibrium was thrown heavily over to the direction of carbon monoxide. Hence, at temperatures greater than 900°C the atomization step would involve the use of hot carbon + carbon monoxide. The system which is illustrated in Figure 1 used an rf coil. This coil induced heat in the carbon rods or pieces which rapidly attained a temperature of 1200-1400°C, according to the power of the radio frequency (rf) generator used. The advantage of using any rf generator as a power source was that the carbon bed was evenly heated across its diameter and that it was rapidly brought to temperature by turning on the rf generator.

In practice ambient air was pulled over the hot carbon bed and reduction to free atoms of metal pollutants in the atmosphere took place. These free atoms issued into the absorption tube. By using the correct system of hollow cathodes and detectors, concentrations of the metal in the atmosphere was calculated from the measured atomic absorption signal.

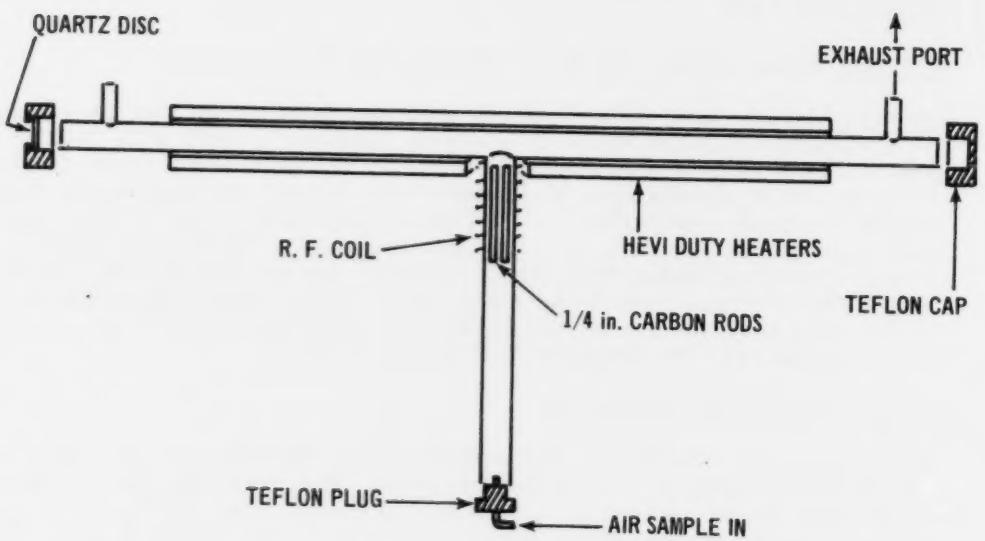


Figure 1. Schematic diagram of the atomizer.

SECTION IV

EQUIPMENT

Optical System and Components. The major components and the optical layout of the equipment are illustrated in Figure 2.

Source. Barnes Demountable hollow cathode

Monochromator Jarrel Ash, Model 82-500, half-meter monochromator

Detectors 1P28, 1P22, R106

Atomizer built during the investigation

Rf generator Lepel 5 kilowatt generator

Amplifier system, PAR amplifier, Model 126 equipped with PAR photometric preamp Model 184.

Recorder Beckman Model 10005 10" potentiometric strip chart.

Optical System. The optical system used was essentially that of single beam optics. Although there is a strong tendency to work with double beam systems in most spectroscopic work, it has been shown that there is very little advantage to the double beam system over the single beam system in atomic absorption. It is seldom possible to put a "reference" sample in the reference beam. The only commercial instrument effectively employing double beam optics employs pseudo-double beam optics where the reference beam is an empty path. Under these circumstances it was felt that there was not sufficient advantage to the double beam system to justify its incorporation in the system.[1]

Construction of the Instrument

Hollow Cathode. The Barnes Demountable Hollow Cathode was preferred to sealed hollow cathodes for several reasons. The first was that having bought the Barnes system for approximately $1,000, new hollow cathodes can be purchased for approximately $10 each. This is an important consideration when it is intended to examine many elements in the periodic table. The alternate route of using sealed hollow cathodes and the necessary power supply would present a smaller initial cost. The power supply can be bought for approximately $500, and the individual hollow cathodes cost approximately $150 each. But, a study involving twenty elements would necessarily require the purchase of twenty different hollow cathodes to provide at least one of the cathodes for each element. It is well known that sealed hollow cathodes have a finite life which may end without warning. This breakdown may hold up work for weeks and perhaps months under some circumstances. The problem was avoided by using demountable cathodes. These can be fabricated in the lab. Hence, these hollow cathodes are cheaper and better to use than sealed lamps.

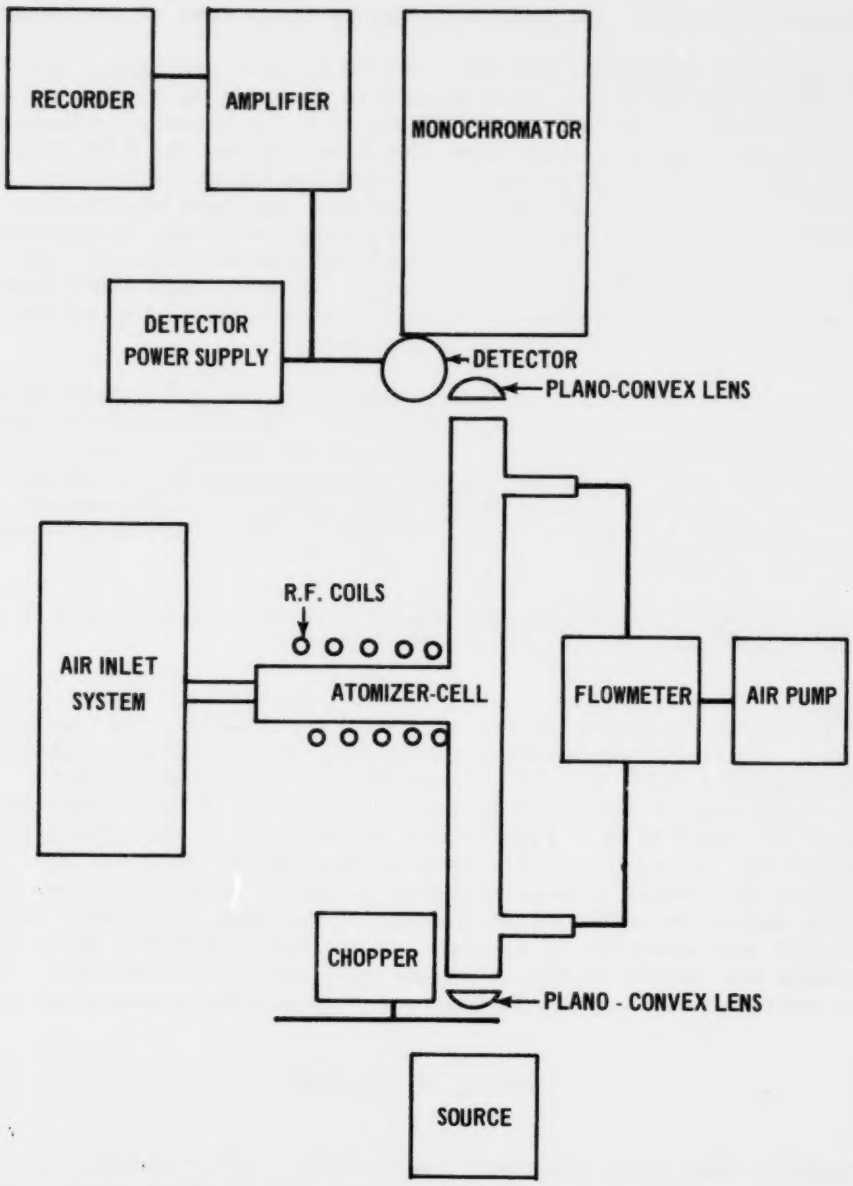


Figure 2. Schematic diagram of equipment.

Monochromator. A Jarrell Ash Model 82-500 half-meter monochromator with grating and adjustable slits was purchased from Fisher Scientific. The monochromator was fitted with an inlet and exit port to allow flushing with nitrogen or argon. This was an important feature if work on elements with resonance lines at wavelengths less than 2100 Å is anticipated, because removal of oxygen from the monochromator was necessary for all such elements. These elements included mercury, arsenic, selenium and sulfur. Our intention was to study some of the elements.

Detector. The detectors used were the 1P28, 1P22 and R106. The response curves of two of these detectors is shown in Figure 3. As can be seen, it was an advantage to use the 1P28 for elements with resonance lines at wavelengths greater than 2100 Å and to use the R106 detector for studies involving elements with resonance lines shorter than 2100 Å. The 1P22 was used for studies of potassium. The housing for the photomultiplier in the Jarrell Ash instrument was completely surrounded by metal and it was felt that this would shield it from any stray radiation from the rf generator and coil. It was found later that this was an erroneous assumption and special precautions had to be taken to shield the monochromator from this radiation.

Amplifier. The amplifier used was a PAR amplifier Model 126 equipped with PAR Photometer Preamplifier Model 184. The unit could be operated as a "Lock-In" amplifier or as a wide band AC amplifier over the range 0.2 Hz to 210 kHz. Since the output from the detector and amplifier system was in the range 0-10 volts, this necessitated the use of a helipot to match the PAR amplifier to our recorder which has a maximum input level of 100 mV.

Read-out System. The read-out system used was the Beckman Model 10005 10 in. potentiometric Strip Chart Recorder.

Atomizer. The most important instrumental development to be accomplished was the construction of an efficient atomizer. As has been pointed out, the flame atomizer is capable of analytical sensitivities in the range of 10^{-6} to 10^{-8} g. However, as described earlier, indications were a long path system using carbon as the atomizing agent offered the promise of a significant improvement in the efficiency of atomization. It was felt that when air was pulled over the hot carbon rods that this would produce a system of carbon plus carbon monoxide. The hot carbon monoxide, being a powerful reducing agent with chemical energy of approximately 11 electron volts, would probably be sufficient to reduce the metals in most, but not all, inorganic compounds. The first system used is shown in Figure 1. It consisted essentially of

$$[CO]V_d = 11.1 \text{ eV}$$

two quartz tubes with half-inch internal diameter joined in the center of one tube to form a T-piece. The short side section had the carbon rods.

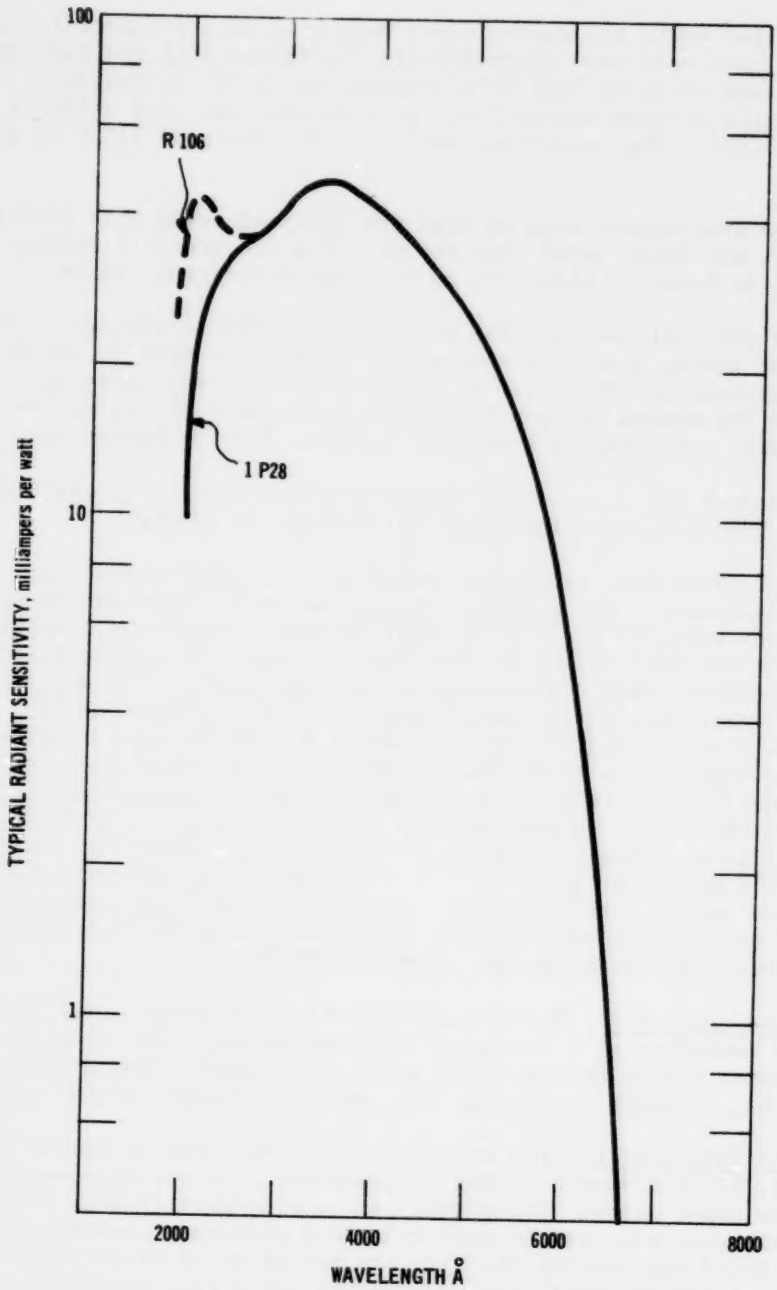


Figure 3. Response curves of the photomultiplier detectors 1P28-R106.

In the initial work, the quartz tubes were held in a horizontal plane. The carbon rods used were approximately six inches long and laid inside the side piece so as to fill it's crossection as far as possible. Numerous types of spectroscopically pure carbon rods were utilized in this experiment. The analytical data will be presented later in this report.

Much of the preliminary data on lead was obtained using this design. However, it was found later that the use of a considerably smaller system was at least as effective as the system described above.

One of the difficulties with the horizontal loading system was that the flowing air sample tended to channel across the top part of the side tube and to burn out that part of the carbon bed preferentially. This meant that the carbon bed was burned out while much of the carbon was still unused, resulting in a reduced lifetime for the carbon bed.

In later models the size of the carbon rods was reduced to small pieces $\frac{1}{4}$" long. The current equipment is illustrated in Figure 4.

It was also found that using the system in a vertical plane held several advantages. For example, it was easier to mount and screen the rf coil thus reducing stray radiation; secondly, since top loading was possible it was much easier to load the bed initially and to refill it during operation since dismantling was not necessary. Thirdly, it was found for later work using liquid samples, that injection of the sample was greatly facilitated by a vertical loading system. When the change was made from a horizontal atomizer to a vertical atomizer, it was also decided to change from carbon rods approximately six inches long to carbon pieces approximately $\frac{1}{4}$" long. As previously indicated the use of long carbon rods increased channeling between the carbon rods as well as at the top of the atomizer system by the incoming air. This caused uneven burning of the carbon and inefficient reduction of the air. When the change was made to carbon pieces the bed became much more uniform and channeling was greatly reduced.

Rf Coil and Generator. The rf generator was a standard Lepel 5 kilowatt generator operating at a frequency of 3 megacycles. The rf coil was hollow copper tubing through which water was pumped. The coil consisted of 10 turns, diameter 35 mm with the total coil length of 120 mm.

Absorption Tube Heater. The absorption tube was made of quartz and, therefore, did not couple to the rf generator. It was necessary to heat it by some other means. The method used was to wind it with nichrome 700 W resistance wire and to cast this in a plaster of asbestos. This was then dried out leaving the side arm heated by an electrical filament. The filament itself was powered off 110 V line together with a variac in order to control the voltage to the filament.

Rf Shielding. In practice it was found that the rf generator and rf coil emitted a considerable amount of rf stray radiation. This

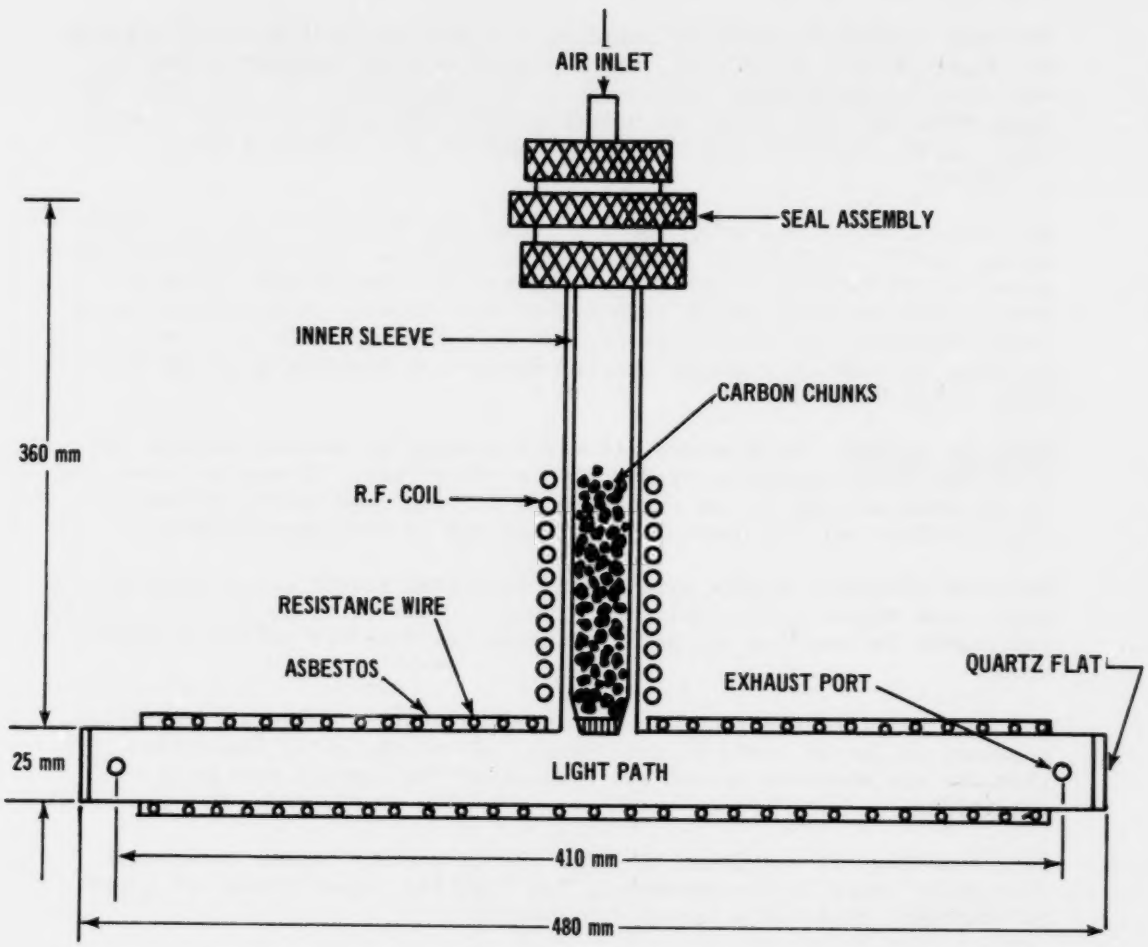


Figure 4. Diagram of current atomizer.

radiation was picked up by many components of the system and led to a very erratic and unstable read-out. Abrupt changes in base line took place for no apparent reason. Also there were slow swings in base line drift and short swings in base line drift producing an inoperable system.

The first approach to correcting this problem was to replace all electrical leads with shielded electrical leads between the various components of the system. This led to some reduction in the background variation, but was not sufficient in itself. Secondly, all components were grounded individually. This, again, led to an improvement in the problem but anytime the rf generator was turned on there was invariably a major change in the signal level of the recorder.

This was finally overcome by building a copper box to completely enclose the atomizer and the rf coil, which prevented stray radiation from the coil from reaching other components of the equipment. In addition, the leads from the coil to the rf generator were enclosed in copper casing. This, again, caused a significant decrease in the stray radiation intensity.

An extra piece of shielding was put around the detector housing. This, again, caused a reduction in background variation. Indications were the normal metal housing of the detector acted as a shield and picked up stray radiation from the rf system, but then became a transmittor, at a lower intensity, of the radiation that it picked up. The problem was overcome by putting a second shield outside and completely around the metal housing system.

Pure Air System. In practice, it was necessary to compare ambient air with some other standard, preferably, a 'pure' air. It was not possible to buy pure air, so it was necessary to provide some system whereby we could produce our own pure air on demand and at a reasonable price.

Numerous scrubbing agents were tried, including nitric acid, hydrochloric acid, aqua regia, silica gel, and alumina. None of these were completely successful in removing the metal contaminates from air pulled through them.

The best purifier was found to be activated charcoal. This effectively removed, as far as could be determined, all of the metal impurities from the air when the system was used under the correct operating conditions.

Unfortunately, it was found that the system rapidly became saturated with water vapor in the atmosphere and that its capacity was not great. In practice, this was a severe disadvantage.

The first attempt to overcome this problem involved heating the carbon to a temperature above 110^{o}C at which point water would not condense and would therefore not saturate the scrubber.

Further studies showed that this system was not satisfactory. As predicted the water was not held very tightly by the carbon and the latter did not become saturated. Unfortunately, other volatile compounds such as mercury salts were also retained by the carbon scrubber at this temperature. The scrubber was not completely satisfactory in providing pure air. The effect of the increased temperature, therefore, was to prolong the life of the carbon purifier, but also made the bed ineffective in removing certain metals from the air.

The problem was later overcome by putting a tube of calcium chloride approximately three feet long in line before the activated charcoal bed. Ambient air was passed through the calcium chloride bed, to remove excessive water and then passed through the activated carbon bed where the metals were removed. Finally a millipore filter stage was added to trap any particulates or carbon dust. This system, in practice, was found to be very successful and provided as easy supply of pure air free of water vapor and metal contaminates. No studies were made on the removal by this train of contaminates such as carbon monoxide or carbon dioxide, because these impurities would not interfere with the system. The system is illustrated in Figure 5.

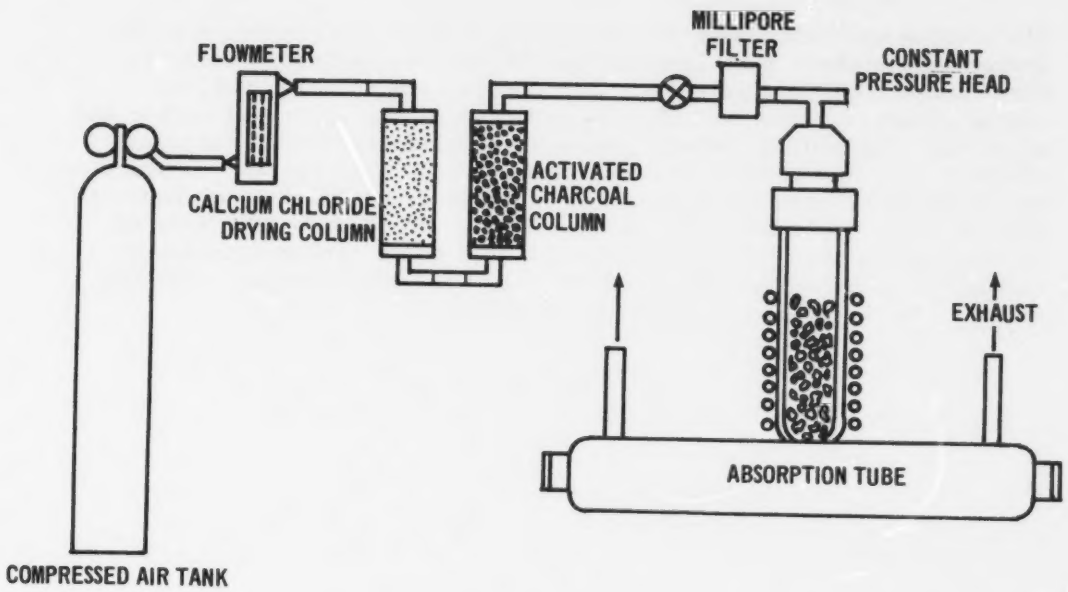


Figure 5. Pure air system.

SECTION V

OPERATIONAL PARAMETERS

The Feasibility of the Method. The first information to be sought was if the system was capable of detecting various metal-containing impurities in the air.

Nine elements were chosen based on their present importance as metal pollutants and their future possible importance in this area. These metals were lead, mercury, cadmium, arsenic, selenium, sodium, potassium, copper, and zinc.

The pure air system was set up so that it could be connected to the entrance port of the atomizer section as desired by turning a glass tap. Alternately, ambient air could be drawn into the system and the signal measured for the particular element being determined.

First, the system was set up with pure air flowing through it. The base line which was presumably zero absorption or at least pseudo-zero absorption was recorded continuously. The source of air was then switched from pure air to ambient air and the absorption signal traced out after a sufficient time to establish a steady absorption signal. The sample was then switched from ambient air to pure air and the signal was measured continuously until it again stabilized.

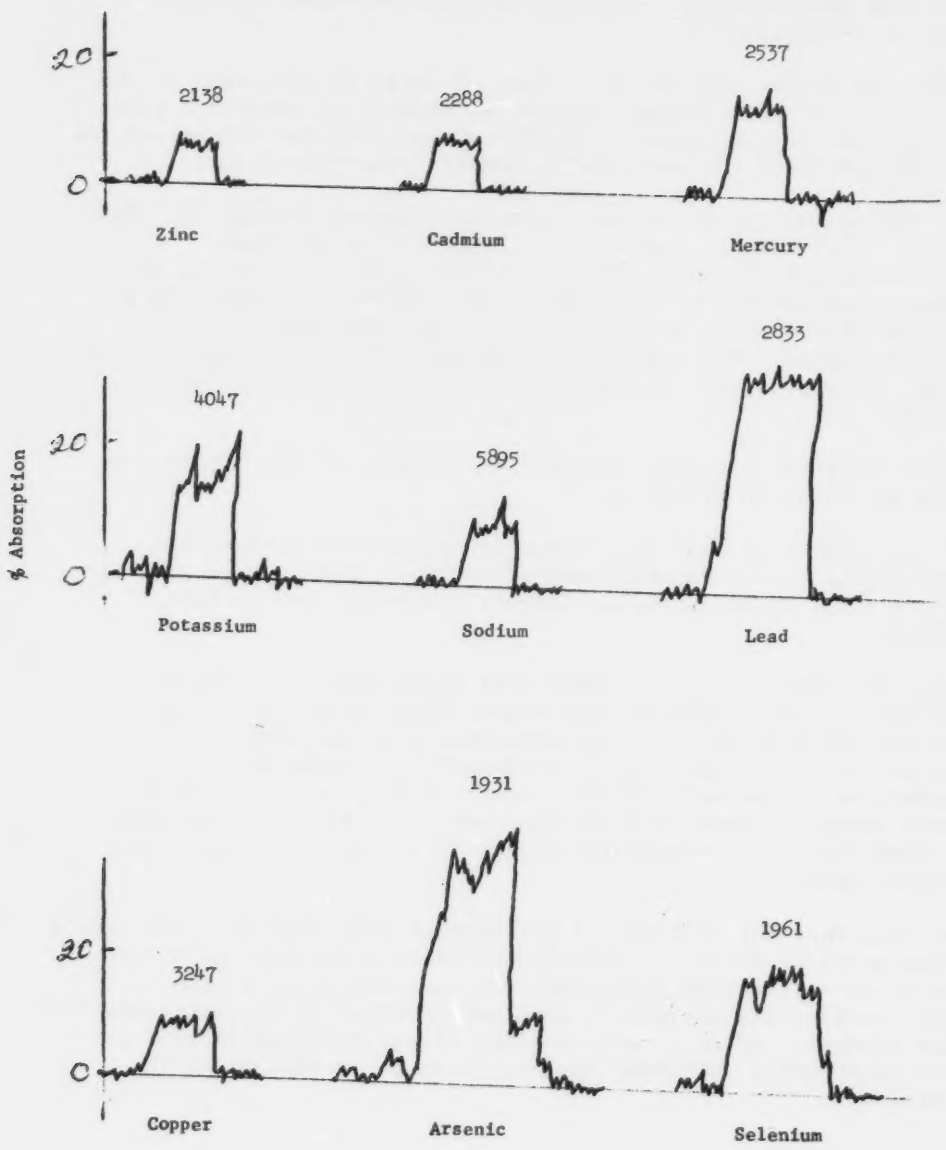
The data obtained were very encouraging. Traces of the absorption spectra are shown in Figure 6.

These data indicated that the method was capable of determining various metals in air directly and it was felt at this time that further studies on producing a reliable analytical system were justified.

One very important observation was that these data were purely qualitative. They indicated that indeed these metals were present in air and could be detected and measured, but the data gave no indication of what these signals represented in terms of metal concentration or how much of these metals were present in the air. The most important problem to be overcome was that of calibration, i.e., translating the absorption signal into concentrations of the particular metal.

It was felt that the problems of calibration were difficult and varied from one metal to another. It was decided that the best approach was to study calibration techniques for one element at a time, thereby learning the analytical problems involved in the determination of that element. After several studies it was anticipated that a general calibration technique applicable to all metals would be developed.

Figure 6. Absorption by Metals in Air (Directly)



For this reason, it was decided to study the element of greatest interest in the air pollution field at this time, i.e., lead.

SECTION VI

THE DIRECT DETERMINATION OF LEAD IN THE ATMOSPHERE

Choice of absorption line. There were two resonance absorption lines for lead. These were at 2833 Å and 2170 Å. The most commonly used line was at 2833 Å. The forte of this line was that it is very stable and easy to work with. From an analytical point of view, it was subject to less interferences from other absorbants in the system and was therefore relatively free from interference, thus generating accurate data. Also the line had a sufficiently high oscillator line to generate high analytical sensitivity for the analysis of most samples.

In contrast, the 2170 Å line had a higher oscillator strength and therefore should be capable of giving better sensitivity. Inasmuch as we felt that we would be striving for sensitivity, it was decided to direct our efforts to the use of this latter line. It was found in practice, that water vapor in the air produced H_2 and CO when passing through the carbon bed. The hydrogen molecules produced absorbed over a broad wavelength range including the 2170 Å line of lead. This absorption produced a direct interference to the method but later it was found that the molecular absorption at wavelengths coincidence with atomic absorption lines could be corrected for and could be eliminated as an analytical problem.

Calibration of Lead. Altshuller Method.[3] The first method used for calibration was that developed by Altshuller. The schematic diagram of the equipment is shown in Figure 7.

Tetraethyl lead (T.E.L.) was placed in the container and weighed accurately. It was then maintained at a temperature of 35.5°C so that tetraethyl lead evaporated off into the air stream which flowed into the equipment. The evaporation rate was such that the lead gave an absorption signal easily measured by the equipment.

The constant temperature was maintained until sufficient tetraethyl lead had been evaporated off to cause a measurable loss in weight of the T.E.L.

In the early experiments, this took approximately 4 or 5 days. However, as the equipment was improved by increasing atomizer temperature, etc., the sensitivity improved by an order of magnitude. This meant that it was necessary to control evaporation of the sample of tetraethyl lead for a period of 40-50 days in order to evaporate off a sufficient

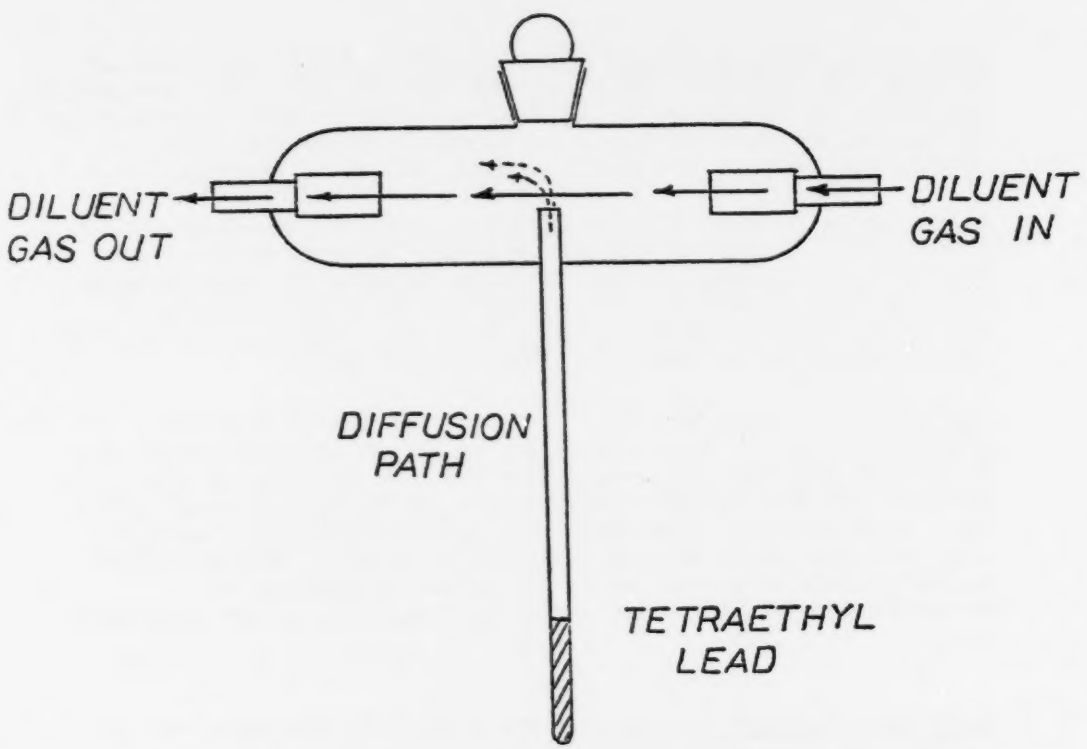


Figure 7. Altshuller Equipment for Calibration with TEL

quantity to weigh. After further improvement by another order of magnitude the time period necessary for evaporation also increased an order of magnitude to between 300 and 400 days.

Clearly the method was now not suitable for calibration of this instrument when it was operated to give high sensitivity.

Another problem with the method was that all material evaporated off during the process was weighed as tetraethyl lead. This included light hydrocarbon impurities present, some of which were evaporated off preferentially but weighed as T.E.L. This generated an error in the procedure which was difficult to evaluate. The technique was not used for further studies.

Calibration Using Compressed Air. The basis of this technique was to pass compressed air from a cylinder into the instrument and measure the degree of absorption by the lead entrained in this compressed air. It was assumed that the sample was homogeneous and that this air measurement would be constant throughout the entire cylinder.

After taking the absorption measurement, the air was passed through a dilute HNO_3 scrubbing solution in which the entrained lead was scrubbed out the sample. The scrubbing solution was then analyzed using spectrophotometric analysis[4] and the lead concentration of the scrubbing solution determined. From this determination the lead concentration in the compressed air was calculated.

One major difficulty with this procedure was that it was time consuming, i.e., it took a whole day to scrube out sufficient air to measure the lead entrained. Also only one datum point was obtained and that was the concentration of the lead in compressed air. A calibration curve could only be constructed by drawing a line from this point through the point of origin. This technique is notoriously dangerous and is not in anyway accurate at concentrations significantly different from those in the compressed air.

Lead Vapor Pressure Techniques. The Altshuller technique for the calibration of lead was based on the fact that tetraethyl lead is a volatile compound. There are a number of other volatile lead compounds available and it should be possible to use the Altshuller technique with these compounds.

Further, it was felt that since the sensitivity of the method appeared to be very high that it might be possible to simply heat up many pure metals and measure the metal that evaporated off into the air stream. Based on literature data on vapor pressure it should be possible to calculate the vapor pressure at the temperatures used of the metal or the metal compound and from that calculate the concentration of metal evaporated during the process.

The compounds tested are listed in Table 1.

The data obtained were very discouraging. First, it was found that many of these compounds decomposed at increased temperature. Many reacted with the hot air which had to be used in order to generate carbon monoxide in the instrument. When the compound decomposed or oxidized in this, the original compound changed chemically and the vapor pressure data were no longer valid. Under these conditions it was impossible to calculate the real vapor pressure of the compound used.

This was even true when pure metal was used because frequently a thin film of molecules was on the metal surface. These molecules were chemically different from the pure metal itself and with a different vapor pressure. Also, the pure metal frequently reacted with the nitrogen or oxygen or other impurities in the air used to pass over the heated metal and again changed chemically, vitiating vapor pressure data.

This calibration method could have been pursued further and used successfully. However, it appeared that the difficulties involved would be extensive and study may have developed into a whole new research project for which little time was available.

It was therefore decided to abandon the use of this technique after preliminary studies.

The Platinum Wire Technique. In this method a platinum loop was incorporated into the entrance of the atomizer system. The equipment is illustrated in Figures 8 and 9.

In this technique a known volume of a solution of the metal under test was spotted onto the platinum wire with a microsyringe. The volume used was in the order of 1 or 2 µl. Any volume greater than this tended to drop off the wire and to provide incorrect data. Any volume less than this was difficult to measure accurately.

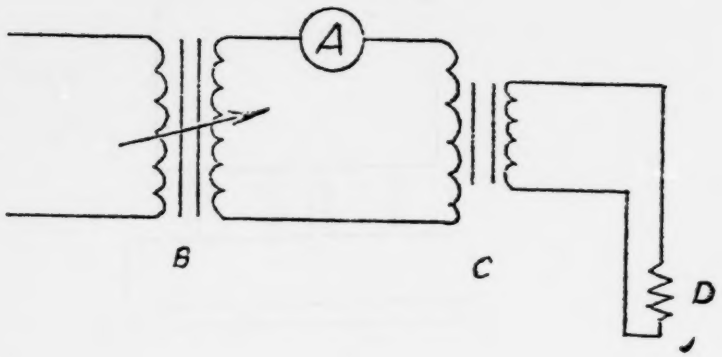
After loading the platinum wire it was lowered into the furnace. The current was then turned on and the platinum wire heated to approximately 2000°C. The heating step took approximately 2 seconds during which time the liquid sample evaporated as did the metal components. The vaporized metal was then swept into the carbon bed and atomized by the flowing air

TABLE 1

Metals and Metal Compounds Used for Calibration Purposes in the Vapor Pressure Technique

Compound	Comment
Arsenic metal	Insufficient temperature control*
Arsenic trioxide	Insufficient temperature control
Cadmium chloride	Successful volatilization
Cadmium sulfide	Successful volatilization
Cadmium sulfate	Successful volatilization
Copper metal	Reacted with trace O_2 in N_2 to give CuO
Copper oxide	Unable to volatilize
Cuprous chloride	Preferential volatilization of impurities
Cupric chloride	Decomposed to CuO
Cupric iodide	Decomposed to CuO
Lead chloride	Successful volatilization
Lead phosphate	Successful volatilization
Lead carbonate	Successful volatilization
Mercuric chloride	Successful volatilization
Mercuric sulfate	Successful volatilization
Mercuric nitrate	Successful volatilization

* Note: Very small changes (e.g., 10°C) caused significant changes in vapor pressure. We were unable to control the temperature this well for the extended time periods necessary to get reliable results.



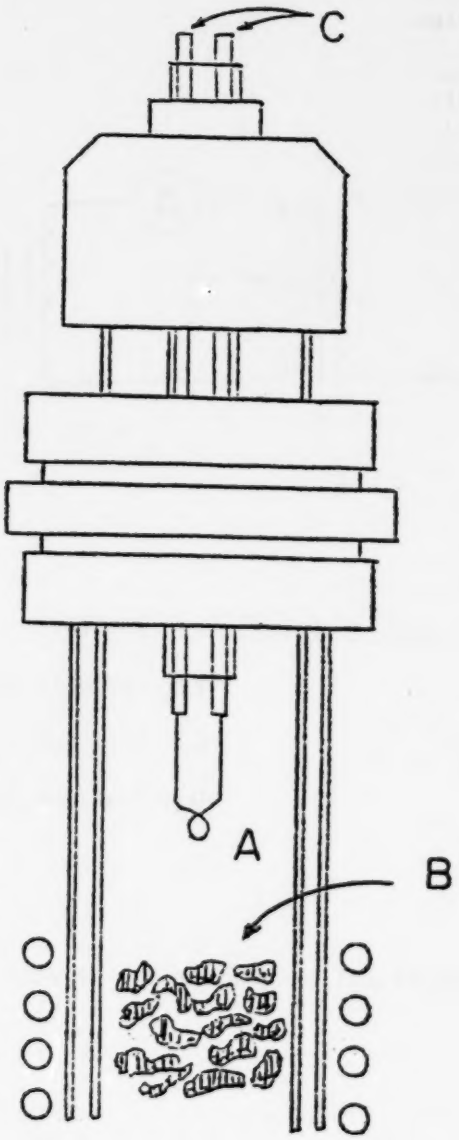
Platinum Loop Injector: A) ammeter

B) variable transformer

C) filament transformer

D) Platinum loop

Figure 8. Electrical Diagram of the Pt Wire Used for Calibration



The platinum loop is at point A immediately above the carbon bed B. The electrical inlets are at point C.

Figure 9. Schematic Diagram of the Pt Wire Calibration Equipment

stream in the normal way. It was assumed that all the sample that was put onto the platinum wire ended up in the furnace and contributed to the absorption signal.

This technique worked well for a number of elements and gave some very informative results. One problem involved was that volatile metals such as lead tended to evaporate at temperatures much lower than that of the very hot platinum wire. Lead was sometimes lost when the platinum wire was lowered into place because of the heat radiated by the bed. Unless the technique was carefully controlled low results were obtained because of this loss of sample by exposure to the hot carbon bed prior to heating the Pt wire. No calibration curves for lead were completed using the Pt wire technique.

Liquid Drop Technique. In this technique a small volume of sample, i.e., 1 to 5 µl was injected onto the hot carbon bed using a microliter syringe. The solution immediately evaporated and the vaporized components were swept through the carbon bed atomizer in the normal way. The equipment is illustrated in Figure 10.

It can be calculated that the 2 µl liquid sample after hitting the bed evaporated to a volume of approximately 10 to 20 cc. This expansion took place extremely rapidly and amounted to a miniature explosion. However, it was found that very little sample was lost during this time and the method was quite reliable and reproducible.

Calibration data were obtained by assuming that all the lead introduced in the sample as a liquid entered the atomizer. Hence, the concentration of lead could be calculated and the degree of absorption correlated with this concentration. It was also assumed that the liquid sample rapidly became gaseous and so approached that of an actual gas or air sample as it entered the atomizer. We believe that this eliminated error caused by different physical types of sample.

The limiting factor of the technique was reproducing the volume of the solution introduced to the sample atomizer. It was difficult to introduce samples of 5 µl reproducibily, i.e., to within an error of 5% using a conventional microliter syringe. Frequently, part of the sample would drop off the syringe tip, leaving a small part of it which stayed on the syringe tip and did not drop off. Instead it evaporated leaving some of the metal behind; in this case a low result was obtained. At other times a sample drop would not fall straight down the column but hit the side of the atomizer. Again, because of the low temperature of the side of the atomizer, slow atomization took place and low results were obtained.

However, the problem was largely overcome by using a Brummond micro pipet modified for positive full displacement. This syringe was capable of reproducing the volume delivered to the atomizer very precisely. Sample volumes of 2 µl were easily handled and reproducible data obtained.

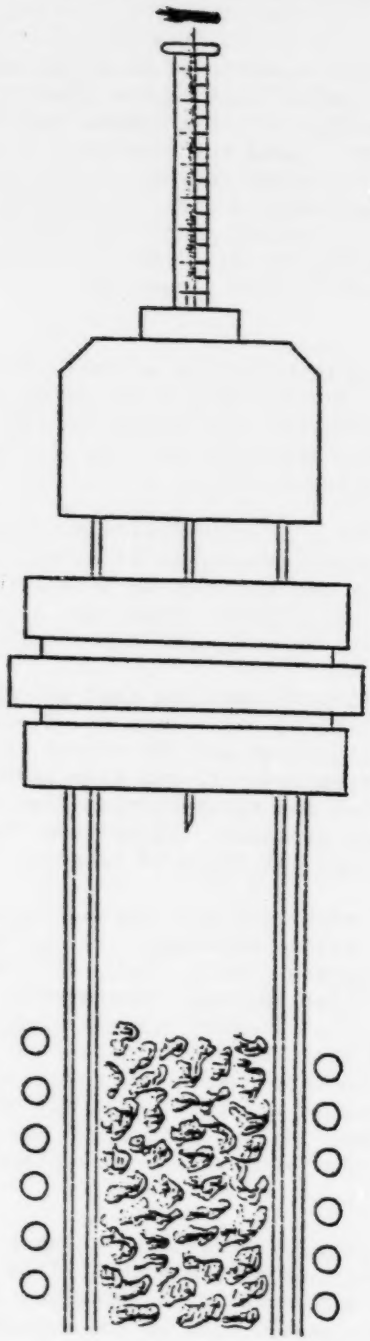


Figure 10. Equipment for Calibration by the Liquid Drop Technique

Contamination on Carbon Rods. The carbon rods as delivered from various manufacturers were tested for metal impurity. It was found that in all cases the lead concentration was sufficiently high to give a full scale deflection immediately after the carbon bed was heated. However, after prolonged heating, i.e., about an hour at 1400°C, the lead evaporated off and the carbon rod became pure enough to give a steady absorption signal which approached zero.

A tracing of typical absorption curves derived from heating the carbon rod is shown in Figure 11. Various types of carbon rods from different manufacturers were tested. The data indicate that the conventional spectrographic carbon rods were far too contaminated to be used under normal circumstances. However, high purity carbon rods were quite satisfactory after suitable cleanup in the equipment for a number of elements tested. Unfortunately, we were not able to cleanup zinc or copper reproducibly.

One other problem with this technique was that frequently lead was reabsorbed from the atmosphere after the rods had been cleaned. This was particularly bad if the instrument was not used for several hours or days. However, the problem was easily corrected by reheating the carbon rods up to temperature and evaporating off the reabsorbed lead until the absorption signal was again steady and approached zero.

Typical Calibration Curves. A typical calibration curve is shown in Figure 12. As can be seen the dynamic range was 0-60 $\mu g\ m^3$.

Data for the Baton Rouge Area. Based on the calibration techniques which were developed and the absorption signals for ambient air in laboratories, the following data were obtained for lead concentrations in Baton Rouge.

Table 2

Concentrations of Lead in Laboratory Air in Baton Rouge

Date	Absorbance	Concentration Pb
8-5-69	.040	1.4 $\mu g/m^3$
9-2-69	.300	15.0 $\mu g/m^3$
10-14-69	.068	2.8 $\mu g/m^3$
11-7-69	.050	2.0 $\mu g/m^3$

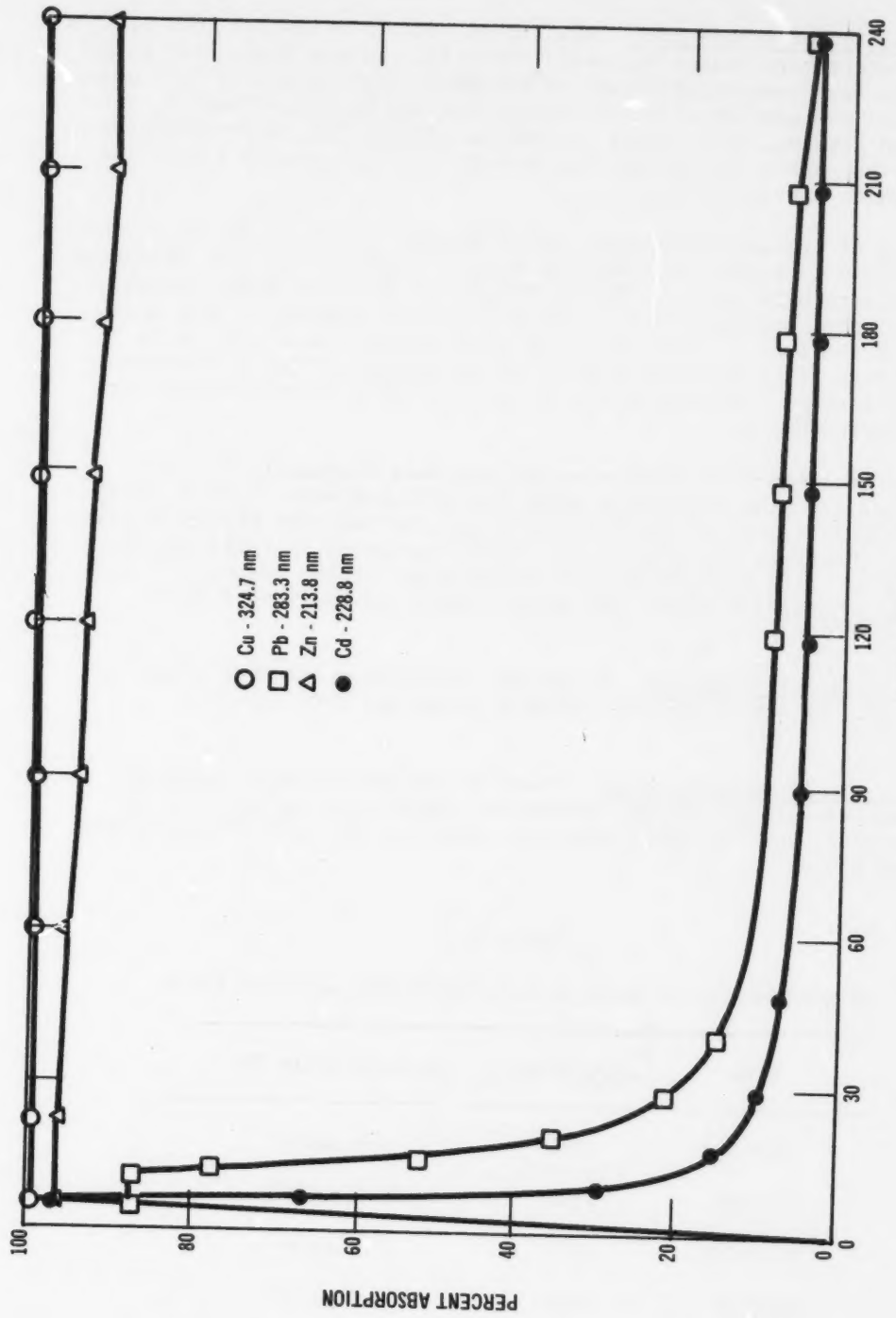


Figure 11. Typical traces of absorption caused by metal bleedoff from carbon rods.

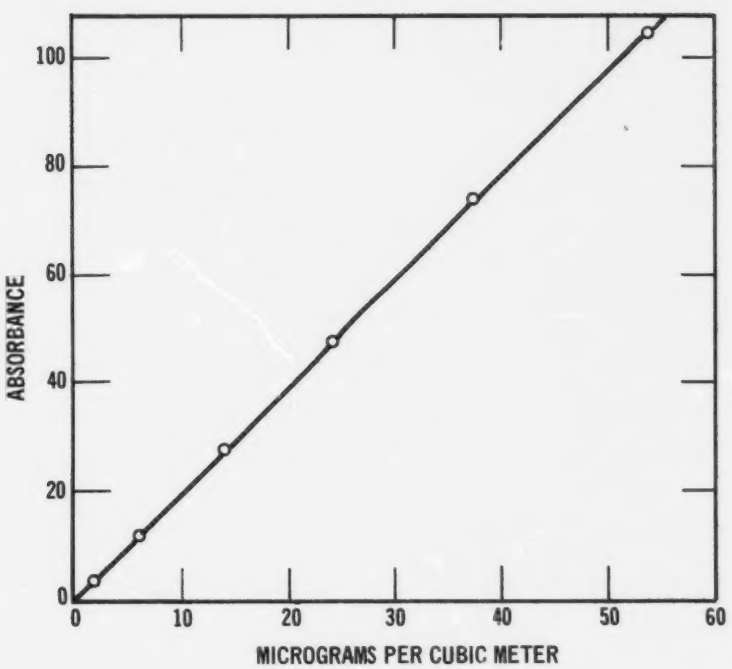


Figure 12. Calibration curve of Pb.

It can be seen that reliable data can be obtained in the concentration range encountered in normal atmospheres. This illustrated that the technique was capable of real time analysis without prior concentration or normal air samples.

Based on the calibration data obtained the sensitivity of the procedure was 10^{-11} g of lead for air samples and based on the calibration data using the liquid drop technique sensitivity for liquid samples was 10^{-12} µg of lead in a 2 µl sample size. The sensitivity in this case is defined as the concentration that gives 1% absorption. The precision of the technique (2 σ 95% confidence) at the 6 $\mu g/m^3$ concentration level was 0.2 $\mu g/m^3$.

SECTION VII

DETERMINATION OF MERCURY IN THE ATMOSPHERE

The next element chosen for study was mercury. This element was chosen for three reasons: first, it is a very important metal pollutant in the atmosphere, it is known to be highly toxic, even at low levels. Second, it is known that mercury has been detected by atomic absorption at low levels and it therefore appeared feasible that this instrument could be applied to reducing the level sufficiently low to enable direct analysis of mercury in the atmosphere. All current methods involved in the determination of mercury require a pre-concentration step followed by analysis by one of several conventional methods. The third reason was that the best resonance line for mercury was at 1849 Å. Hitherto, most of the work carried out on the determination of mercury has been made by using the resonance line at 2533 Å. The oscillator strength of the 1849 Å line is approximately 50 times as strong as the 2533 Å line. It is, therefore, reasonable to assume that the detection limit at 1849 Å would be at least an order of magnitude better than the detection limit at 2533 Å.

In addition to this, the investigation of the use of the line at 1849 Å would provide the extra challenge of having to work in the vacuum ultraviolet region of the spectrum. A number of elements have very intense absorption lines in the vacuum ultraviolet. These elements include arsenic, selenium and sulfur, all of which are very important in the field of air pollution. Their determination has been difficult in the past because of lack of sensitivity. It was, therefore, considered to be an attractive challenge to work in the vacuum ultraviolet and study the problems involved in the use of this part of the spectrum. It was hoped that by successfully solving these problems the determination of arsenic and selenium would be much easier than the present status of affairs.

Direct Determination of Mercury in the Atmosphere. By drawing ambient air through the instrument it was possible to detect absorption signals caused by mercury present in the air. Typical absorption traces are shown in Figure 6. The data showed that it was experimentally possible to measure the absorption signal caused by the presence of mercury in the air. This data proved that mercury could be determined directly using this equipment. It remained to calibrate the signal by one of the techniques already developed for lead and to correct the signal for molecular absorption in the vicinity of the mercury line.

Calibration Procedure. Mercury was one of the easier metals to handled inasmuch as it is readily volatile at low temperatures and it is available in fairly pure chemical form. Two approaches were taken to the calibration problem, one was to enclose mercury metal in a well-stoppered bottle and allow the metal to come to equilibrium with mercury vapor above it. The temperature of the partially filled bottle was rigidly monitored. After a suitable length of time a known volume of the air above the mercury was extracted using a syringe. The weight of mercury in the volume extracted was calculated based on the vapor pressure of mercury metal at the temperature used. The air withdrawn from the bottle was then injected as a slug into the equipment by way of the pur air stream entering the carbon bed. This is illustrated in Figure 13. The mercury metal travelled through the carbon bed and into the absorption tube. Here the absorption signal was measured in the normal way.

By varying the volume of mercury and air withdrawn from the bottle and injected into the sample train the weight of mercury injected into the equipment could be varied. Using this technique the relationship between the absorption signal and weight of mercury was determined by the standard procedure.

The second technique used was to inject the mercury vapor continuously over a relatively slow time period of several minutes into a flowing air stream. The mixture of Hg and air provided a continuous absorption signal. By varying flow rates the mercury concentration was varied. The equipment is illustrated in Figure 14.

Results of Calibration Experiments. The early results of this experiment were very disappointing in that they indicated the absorption by mercury using the 1849 Å line was not particularly good. Moreover, it was not better than the absorption found using the 2533 Å line, which was in conflict with theoretical predictions. It was concluded at this time that we were operating under some incorrect experimental conditions; therefore, we continued to study this problem with the hope of elucidating the reason for the low sensitivity.

One of the salient features of the calibration curves was the very flat relationship between the degree of absorption and quantity of mercury introduced into the AA instrument.

This kind of data was typical of that obtained when the line source of the hollow cathode was self-reversed.

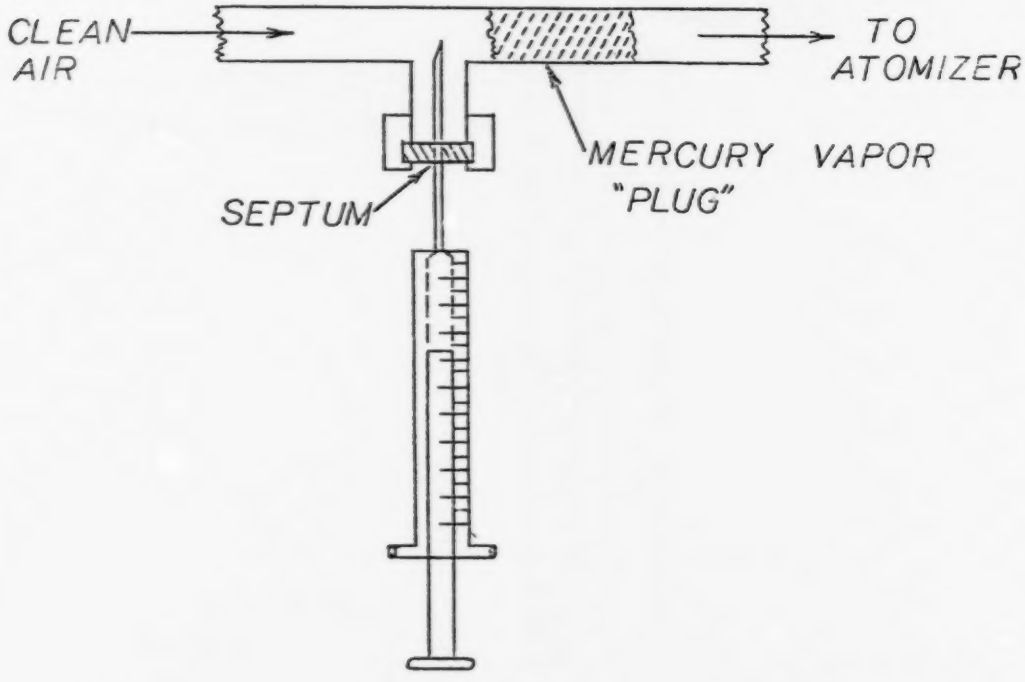


Figure 13. Plug Injection of Hg Used for Calibration

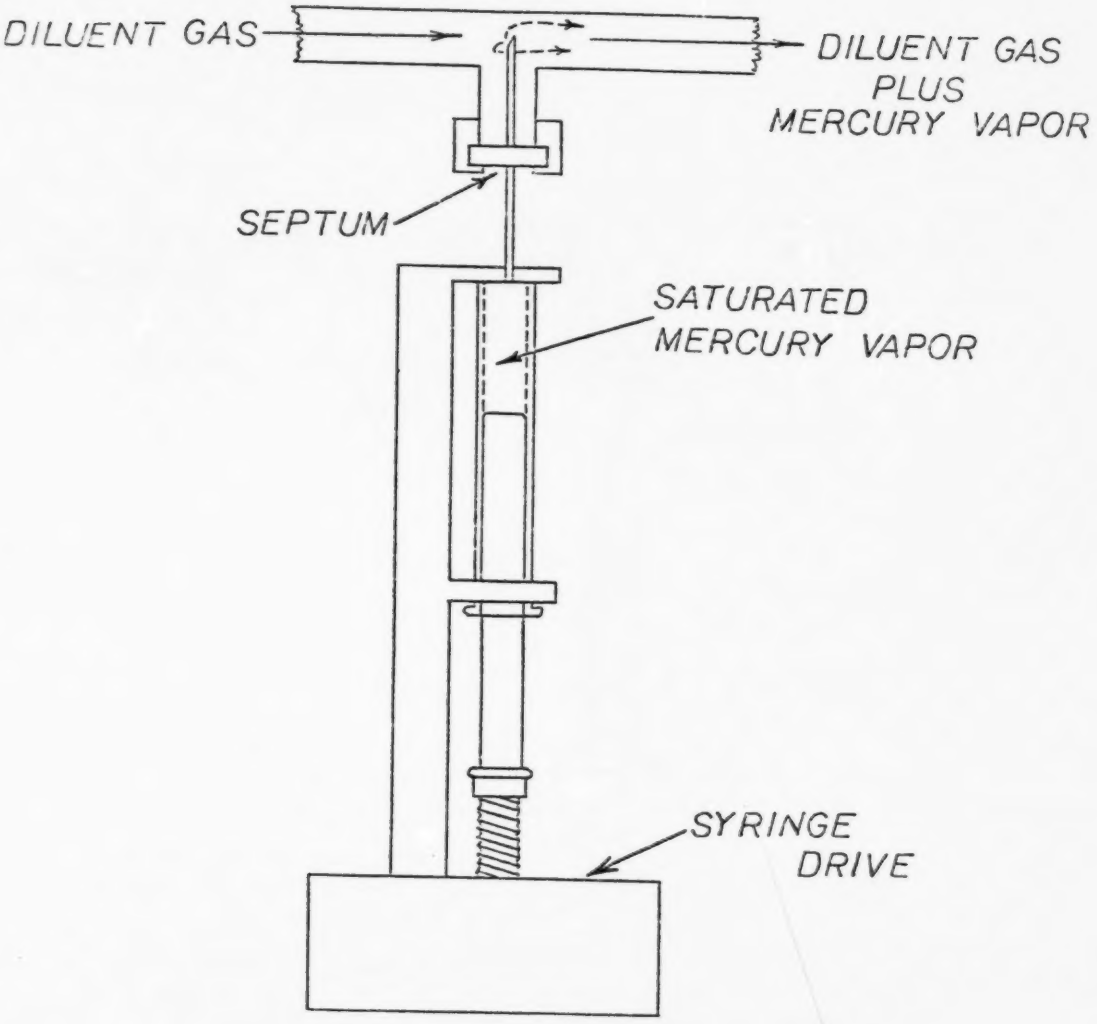


Figure 14. Continuous Injection of Hg for Calibration

Under these conditions, the hollow cathode itself generated a cloud of free mercury atoms which float in front of the cathode discharge. Free atoms absorb the very center of the emitted resonance line.

The linewidth of the emitted resonance line was somewhat less than 1/10th of an angstrom. Not all of this line can be absorbed by free atoms in the light path. In fact, normally only a linewidth of about .01 of an angstrom would be absorbed by free atoms. It should be noted that the actual linewidth absorbed depends on the temperature of the absorbing atoms; increasing temperatures causes an increase in the linewidth absorbed. However, the heart of the emission line is that part which is most easily absorbed by free mercury atoms. If this part of the emission line is absorbed in the hollow cathode, then it is not possible for it to be absorbed by free metal atoms in the sample.

The net result was that although the hollow cathode appeared to be emitting at its resonance line, in fact the center of the emitted line had been absorbed in the lamp itself, i.e., the line was reversed. Under these circumstances, the mercury atoms in the sample could only absorb a little radiation no matter what was the concentration of the metal atoms. The net result was a flat calibration curve similar to those obtained in our first experimental studies.

Several other types of lamps were used for preparing calibration curves. It was found in each case that if a sealed lamp was used that the calibration curve was very flat and not particularly useful for the analytical determination of mercury.

However, when the Barnes demountable hollow cathode was used, a much steeper relationship between absorption and metal concentration was obtained. The Barnes demountable hollow cathod was not sealed. Rather the filler gas flowed steadily through the cathode itself, when in use. Under these circumstances any mercury vapor which was generated by sputtering of the hollow cathode was not allowed to accumulate inside the cathode itself, but was swept out with the filler gas during its normal functioning operation.

The degree of self-reversal was very much reduced and the heart of the resonance line was left relatively unabsorbed by the lamp itself.

Typical calibration traces using different types of mercury lamps are illustrated in Figure 15. It can be seen that the Barnes demountable hollow cathode was much more successful in application than any of the other sources routinely used. It should be noted, however, that this difference in calibration curve was not noted to the same degree when the 2533 Å resonance line was used. This was because the oscillator strength of the 2533 Å line was much less than the 1849 Å line and self-reversal was much less of a problem because entrapped mercury metal in the sealed hollow cathode absorbed out a much smaller fraction of the resonance line used.

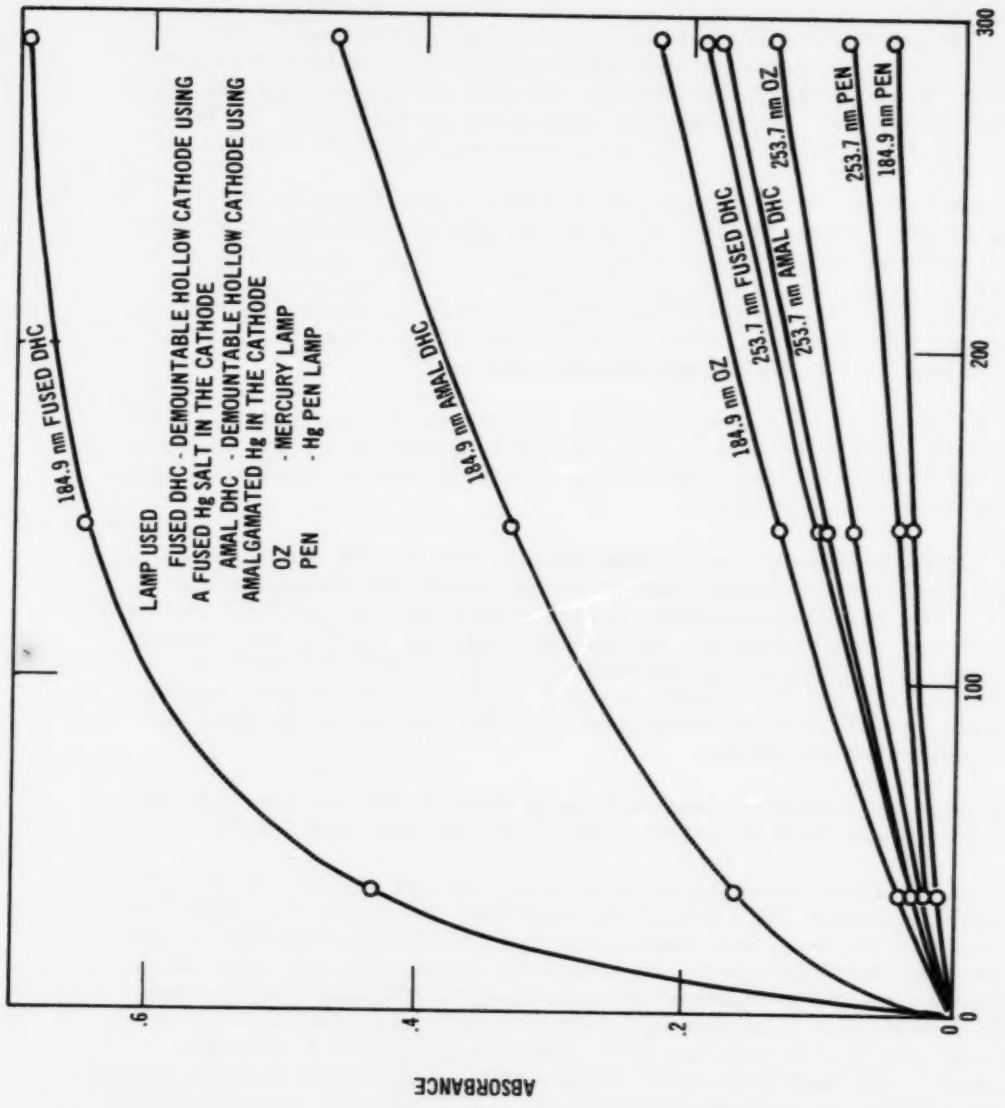


Figure 15. Calibration curves of Hg with different sources.

It was concluded that if mercury were to be determined with the maximum sensitivity that the 1849 Å line should be used because of the higher oscillator strength of this line. But, an unsealed hollow cathode such as the Barnes demountable hollow cathode must be used in order to avoid self-reversal problems encountered in sealed mounts.

Correction for Molecular Absorption. At 1849 Å there were a number of compounds which might absorb quite strongly. Included in these were water, oxygen and hydrogen. Under normal operating conditions, all oxygen in the air was burned to carbon monoxide. All water in the air was converted to carbon monoxide and hydrogen, but any organic material in the air was converted to carbon monoxide and hydrogen leaving a significant amount of hydrogen in the gas phase. It was important, therefore, to correct for the variable amount of hydrogen present after the wet air had passed through the atomizer.

Correction for Molecular Absorptions at 1849 Å. The procedure used for making this correction was to take a hydrogen lamp or a deuterium lamp which emitted broad band radiation at the wavelength of the mercury resonance line 1849 Å.[5] The instrument was tuned to the resonance wavelength using the Barnes demountable mercury cathode. This cathode was then replaced with a deuterium lamp and the wavelength setting held constant. The spectral line width of the monochromator slit system was kept at 1.25 Å, hence this was the width of the wavelength range falling on the detector. The absorption line width of mercury atoms was approximately 0.01 Å wide. Because the absorption line width was extremely narrow compared to the emission line width, the mercury atoms could only absorb a small amount of the light falling on the detector. Even if the system was saturated with mercury atoms, the total amount of light falling on the detector would be decreased by an exceedingly small amount.

For example, suppose the spectral line width was 1 Å wide and the mercury absorbed out of this a line of .01 Å wide, then with complete absorption of that narrow band this signal would decrease by 1%. This is a very small change in signal and probably within the accuracy of the equipment being used.

On the other hand, molecular absorption is invariably broad-band and any absorption by hydrogen at 1849 Å would take place over the entire band width falling on the detector, in this instance 1 Å.

Absorption of Broad-band Radiation (1 Å) by Molecules and by Atoms

Initial signal I_0	100 units
% Absorption by H_2 molecules (molecular absorption)	20%
Bandwidth	1 Å
Net signal (I_0-mol absorption)	80 units
% Absorption by atoms	30%
Bandwidth	0.01 Å

i.e., 30% of the 80 units is absorbed over a bandwidth of 0.01 Å, but none of the 80 units is absorbed from the remaining 0.99 Å

∴ Net reduction in broad band signal by atoms is

$$80 \times \frac{30}{100} \times \frac{0.01}{1.00} = .024\%$$

∴ Net signal after absorption by molecules and atoms = 80 - 0.024

i.e. 79.976

It can be seen that even with relatively strong atomic absorption that the absorption of radiation from the deuterium lamp was to a first approximation, a fairly accurate measurement of the molecular absorption at that wavelength. This means that by measuring the background absorption using the deuterium lamp, molecular absorption could be measured directly without significant interference by atomic absorption even at the same wavelength.

In contrast, when the mercury hollow cathode lamp was used, then not only did the mercury atoms absorb strongly at the resonance line, i.e., 1849 Å, but also molecular absorption by hydrogen took place.

Under the conditions indicated in the illustration above, the degree of absorption by the hydrogen molecules would be 20% of the resonance line and of the mercury lamps would be 30% of the remaining radiation.

Initial signal	100 units
Absorption by molecules 20% unabsorbed signal (I_0 - mol absorption)	80 units
Absorption by atoms 30% i.e. $\frac{80 \times 30}{100}$ units =	24 units

Final signal 80 - 24 = 56 units

Total absorption by atoms and molecules 100 - 56 = 44%

It can be seen, therefore, that the absorption of the resonance line emitted by the hollow cathode lamp was attenuated by atomic and molecular absorption whereas the absorption of the deuterium lamp was, to a first approximation, only that of the molecular absorption. By subtracting absorption of the deuterium lamp from that of the hollow cathode the atomic absorption at that wavelength could be calculated. This permitted a direct correction for molecular absorption to be made.

Equipment Used. In order to measure the absorption of the resonance line in the vacuum ultraviolet at 1849 Å, it was necessary to remove oxygen from the light path. Oxygen absorbs at wavelengths shorter than 2000 Å. Also, it is known that nitrogen begins to absorb at wavelengths less than 1850 Å.

In order to eliminate most of the problem due to air absorption, the monochromator was purged with Argon. Indications were this would completely eliminate any absorption by oxygen, which was significant, and any small absorption by nitrogen.

The Jarrell Ash instrument used was fitted with purging inlet and outlet taps and Argon was blown through the system for approximately ten minutes before measurements were taken. This purging resulted in a significant decrease in absorption due to air and a consequent increase in the intensity of radiation falling on the detector. This is always an advantage since under these conditions the amplifier and the photomultiplier can be operated at lower currents with a consequent improvement in the noise level of the signal generated.

It should also be noted that the absorption cells used contain hot nitrogen from the air and carbon monoxide derived from oxygen in the air. It was found in practice that the molecular absorption was approximately 15 to 20% and that we could operate under these conditions.

There were small air gaps in the equipment between (a) the hollow cathode and the absorption tube and (b) the absorption tube and the inlet system of the monochromator. In practice it was found that the degree of absorption by these air gaps was sufficiently small to permit reasonable signals to reach the detector. No steps were taken to eliminate these air gaps.

Results. Calibration data was obtained using the slug injection system. After making corrections for molecular absorption due principally to water in the atmosphere, the following data were obtained for mercury in the laboratory atmosphere on the dates cited.

Table 3

Mercury Concentrations in the Laboratory Air (Baton Rouge, La.)

Date	Mercury Concentration ($\mu g/m^3$)
3-3-72	14
3-7-72	30
3-7-72	8
3-8-72	15
3-9-72	10
3-13-72	5
3-14-72	1

It should be noted that these mercury levels were quite high, significantly higher than that which is normally obtained in outside atmosphere. However, it should be remembered that the "ambient atmosphere" which was analyzed was that of a laboratory and it is quite common for the mercury levels in chemical laboratories to be significantly higher than that found in outside air.

Conclusions. The procedure developed clearly indicated that mercury could be determined in the atmosphere directly and in real time.

Care must be taken to correct for atmospheric humidity variations and positive steps must be taken to use the correct type of hollow cathode in order to avoid self-reversal problems. However, neither of these complications are difficult to overcome in practice.

The sensitivity (1% absorption) obtained for mercury was 10^{-12} g based on 0.1 $\mu g/m^3$ of air and sampling 30 ml. Typical data are shown in Table 4 and Table 5.

TABLE 4

Analytical Precision of Plug Injection Calibration Technique

Injection Number*	Absorbance	Deviation
1	0.184	0.008
2	0.185	0.009
3	0.175	0.001
4	0.178	0.002
5	0.176	0.000
6	0.162	0.014
7	0.170	0.006
	Mean = 0.176	Standard Deviation = 0.009

* 10 cm^3 of saturated vapor at 20°C

TABLE 5

Analytical Precision of Continuous Injection Calibration Technique

Injection Rate	Absorbance	Deviation
1 cm^3/min @ 20°C	0.452	0.007
(13.2 $\mu g/m^3$)	0.608	0.149
	0.487	0.028
	0.463	0.004
	0.354	0.105
	0.367	0.008
	0.416	0.043
	0.526	0.067
	Mean = 0.459	Standard Deviation = 0.076
0.66 cm^3/min @ 20.8°C	0.410	0.014
(9.3 $\mu g/m^3$)	0.386	0.038
	0.506	0.102
	0.438	0.014
	0.413	0.011
	0.390	0.034
	Mean = 0.424	Standard Deviation = 0.052
0.25 cm^3/min @ 22°C	0.392	0.046
(3.9 $\mu g/m^3$)	0.348	0.002
	0.227	0.119
	0.363	0.017
	0.435	0.089
	0.250	0.096
	0.256	0.090
	0.496	0.150
	Mean = 0.346	Standard Deviation = 0.096

SECTION VIII

DETERMINATION OF CADMIUM IN THE ATMOSPHERE

The next element chosen for study was cadmium. This element is known to be highly toxic and is of increasing importance in pollution studies. It was also known that the concentration levels in the atmosphere were extremely low, i.e., in the order of .01 to .1 micrograms per cubic meter of air. The current methods of analysis were to scrub out the cadmium from the atmosphere and to determine the metal by conventional colorimetry or flame atomic absorption spectroscopy.

The research approach taken was the conventional approach now developed by this technique, i.e., the air was drawn into the atomizer and cadmium absorption at 2288 Å was measured. Samples of ambient air produced a cadmium absorption signal indicating that the procedure was sufficiently sensitive to measure the cadmium in the air directly by this technique.

EQUIPMENT. The equipment used was similar to that illustrated in Figure 2. The components were as follows: RF Generator - Lepel Model. Monochromator - Jarrell-Ash ½ Meter Ebert. Detector and Read-out System - IP28A photomultiplier tube. Jarrell-Ash broad band AC amplifier and Beckman 10" stripchart recorder. Optics - Suprasil Phano-convex Quartz Lenses, 10 cm focal length, and suprasil ½" diameter quartz Flat Cell Windows. Optical Pyrometer - Leeds and Northrup Company. Filament Transformer - General Electric 34J243 110 V input - 6.3 V output. Variable Transformer - Staco Inc. 2PF751 0-8 amps rated.

Air Sampling Network - compressed air tanks, input rotameter, calcium chloride scrubber, activated charcoal scrubber, millipore filter, and constant-pressure sampling head.

Platinum Loop Liquid Injector - variable transformer, ammeter, filament transformer, and 20 gauge platinum wire loop.

Direct Drop Liquid Injector - Hamilton 10 microliter syringe with 3" needle.

Chemicals and Solutions. Cadmium stock solution (1000 μg/ml) was prepared by dissolving 1.000 g Cd metal (A. D. Mackay and Co.) in the minimum volume of concentrated hydrochloric acid and diluting to 1000 ml with 1% (V/V) HCl. More dilute solutions were made up daily by dilution of 1000 μg/ml stock solution with distilled water. All solutions were stored in polyethylene bottles and vials. No solutions were stored overnight in order to avoid plating out problems.

Calibration Techniques. Several calibration techniques were investigated in order to correlate the absorption signal from cadmium in the atmosphere and the concentration of cadmium in the air. Although cadmium itself is relatively volatile compared to most metals, its salts are not particularly volatile. In addition the metal is quite chemically reactive at elevated temperatures. This precluded the method of evaporating cadmium or cadmium salts into the air stream as the basis for a calibration technique.

The successful techniques developed were (a) platinum wire technique and (b) the liquid drop technique.

Platinum Wire Technique. A platinum wire was built so that it could be inserted into the air stream immediately before reaching the furnace. This procedure is described earlier under the section on lead. (See Figure 8 and 9.)

Several cadmium solutions were made up, each with a known concentration of cadmium. A fixed quantity of the cadmium solution was placed onto the platinum wire using a standard capillary. In this instance, the volume used was 5 µl. The platinum wire with the 5 µl of solution was lowered into the atomizer cell, with the air stream gently flowing at a predetermined rate over the wire. The platinum wire was heated by a separate electrical circuit to a bright white heat, i.e., about 2000°C. The cadmium solution rapidly evaporated and the cadmium atoms were swept through the furnace into the absorption cell. By using different concentrations of cadmium, the quantity of cadmium introduced into the cell was varied. The absorption signal for each cadmium concentration was measured and a calibration curve obtained. A typical calibration curve is illustrated in Figure 16.

Calibration Using Liquid Drop Technique. In this system a drop of solution 2 µl in volume was dropped directly into the atomizing bed. Here the drop evaporated rapidly. The liberated cadmium atoms were swept into the absorption tube and the absorption measurement made in the normal way.

In the preliminary work the difficulty involved with this technique was that the volume of solution introduced into the bed was fairly difficult to reproduce. The drop would sometimes fall off the tip of the syringe leaving a small part behind, or some evaporation of the drop took place leaving a small residue of cadmium metal on the tip of the needle. In either case, a low result would be obtained. Unfortunately, the residual metal would then cause a high result with the next drop, the data obtained in this fashion being very inprecise.

The problem was solved by using a Drummond micro pipet modified for full displacement. In this type of pipet liquid in the bore of the syringe was completely displaced by the needle pushing all of the liquid out of the tip by air displacement and forcing it to be ejected into the

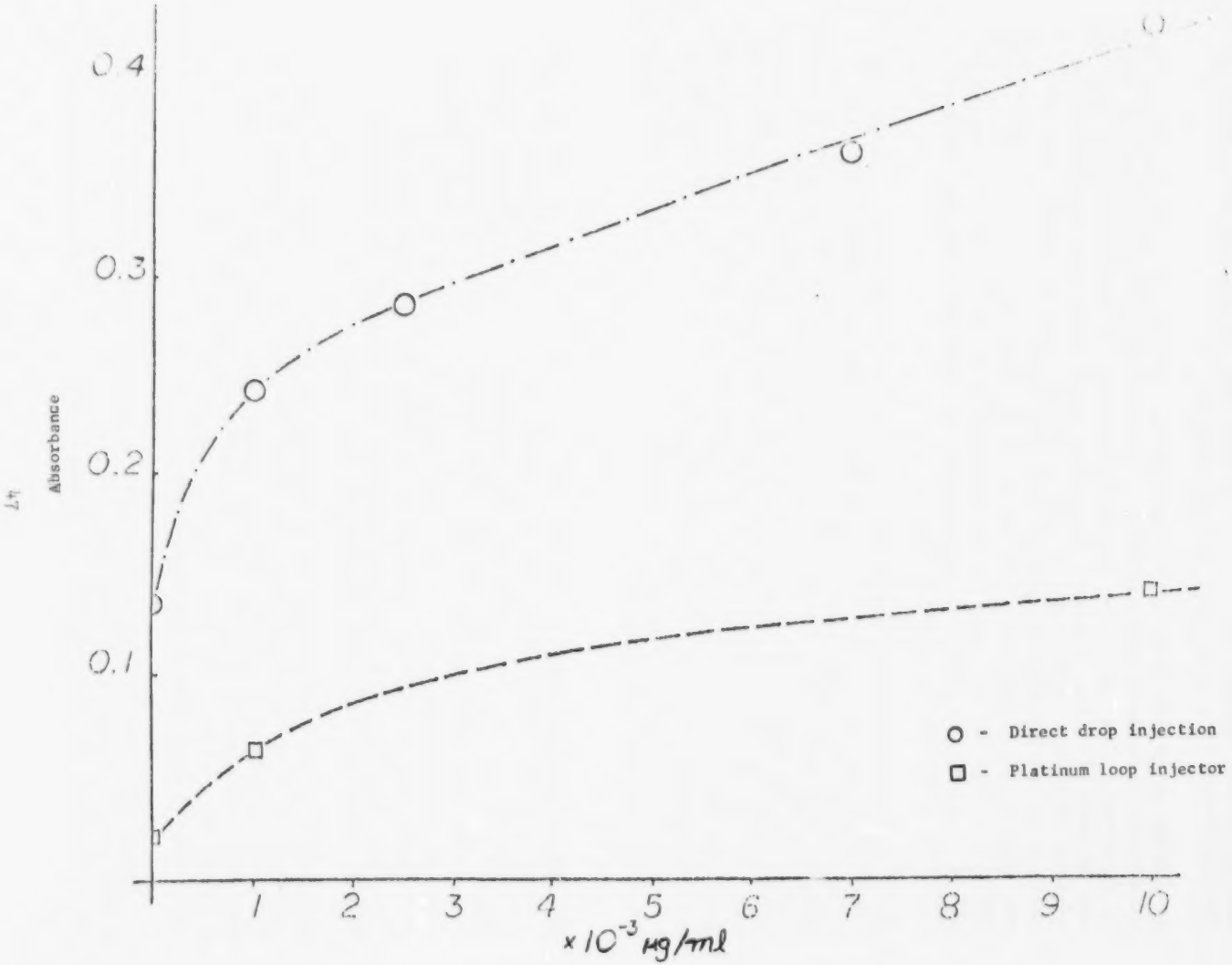


Figure 16. Calibration Curves of Cd (Pt Loop) and Liquid Drop

atomizer. There was an significant increase in the precision of the procedure and sample volumes could be decreased quite safely from 5 µl to 2 µl and still get precise data. It was much easier to handle this volume of sample since when it hit the hot atomizer bed invariably the evaporation took place at explosive rates and 5 µl generated a significantly greater volume than 2 µl. In practice it was easier to control the explosion of a 2 µl than a 5 µl sample.

By making up standard solutions of cadmium of varying concentrations the relationship between cadmium absorption and cadmium concentrations could be measured. The resulting calibration curve is shown in Figure 16. It can be seen that the slope of the calibration curve was significantly steeper than that obtained when the platinum loop was used. However, if instead of the maximum absorption the peak area was used as a measure of the absorption signal, the two curves coincided much more closely. This indicated that in the case of the platinum wire the cadmium evaporated off at a speed relatively slow compared to when the drop was ejected directly onto the hot carbon bed.

There were advantages and disadvantages to both techniques. When high sensitivity was required, it was better to use the liquid drop technique, since the signal was sharp and could be fairly easily measured. However, if high precision was necessary, it was better to use the platinum wire and measure the area of the curve. The problems involved were typically those of the gas chromogram where the peak height or peak area can be used successfully for quantitative analysis. There was one added difficulty with atomic absorption and that was that the relationship between absorption and concentration was logarithmic, not linear. A correction must be made for the logarithmic relationship of the area in order to get precise results.

The Use of Carbon Discs. Some success has been achieved by the use of carbon rods for analysis of various metals by atomic absorption spectroscopy. In this technique the solution was put onto the carbon rod when it was cold. The rod was then warmed up and the solvent evaporated off and discarded. The rod was then heated to high temperature and atomization took place. The temperature control of this procedure must be rigidly adhered to in order to get reproducible results. It has always been a suspicion that some of the volatile metals could be lost when the solvent was evaporated off.

Cadmium is a typical example of a volatile metal which might be lost during this evaporation stage. In order to check this information the cadmium solution was spotted onto a carbon disc. The disc was lowered into the atomization chamber and the solvent evaporated off into the flowing air stream. The air stream in turn drove the solvent through the atomizer into the absorption chamber.

In the atomization chamber all organic materials were burned to carbon monoxide and hydrogen and any water was also converted to carbon monoxide and hydrogen. It was possible to correct for any molecular absorption

due to hydrogen using the deuterium lamp as described in the mercury section. However, in practice it was found that hydrogen did not absorb significantly at the resonance wavelenght of cadmium, therefore, no correction was necessary for molecular absorption.

A cadmium solution was injected onto the carbon disc, which was then lowered to within two inches of the hot carbon bed. Here the temperature of the disc was approximately 200°C, a temperature comparable to that used in the carbon rod drying step.[8,7] The solvent evaporated off within a relatively short period of time. When the carbon disc was completely dry, it was dropped onto the atomizing system and the absorption due to cadmium metal was recorded. A typical spectrum thus obtained is shown in Figure 17. As can be seen cadmium was indeed lost during the drying stage and the bulk was found during the atomization stage.

This indicated a direct error may be involved in the carbon bed method. However, in the carbon bed technique which we used no drying stage was necessary and no error is involved.

Results. Based on this technique and the calibration curves obtained, typical results for the analyses of laboratory atmosphere in Baton Rouge are shown in Table 6.

Table 6

Typical Cd Concentrations in the Laboratory Atmosphere at Baton Rouge, La.

Sample Date	Absorbance	Concentration ($\mu g/m^3$)
Aug. 24, 1972*	0.027 ± 0.005	0.020 ± 0.004
Aug. 25, 1972**	0.044 ± 0.008	0.035 ± 0.005

* Immediately after heavy rain

** Weather hot, clear, sunny

The sensitivity of the procedure was determined to be 10^{-13} grams of cadmium using the liquid drop technique.

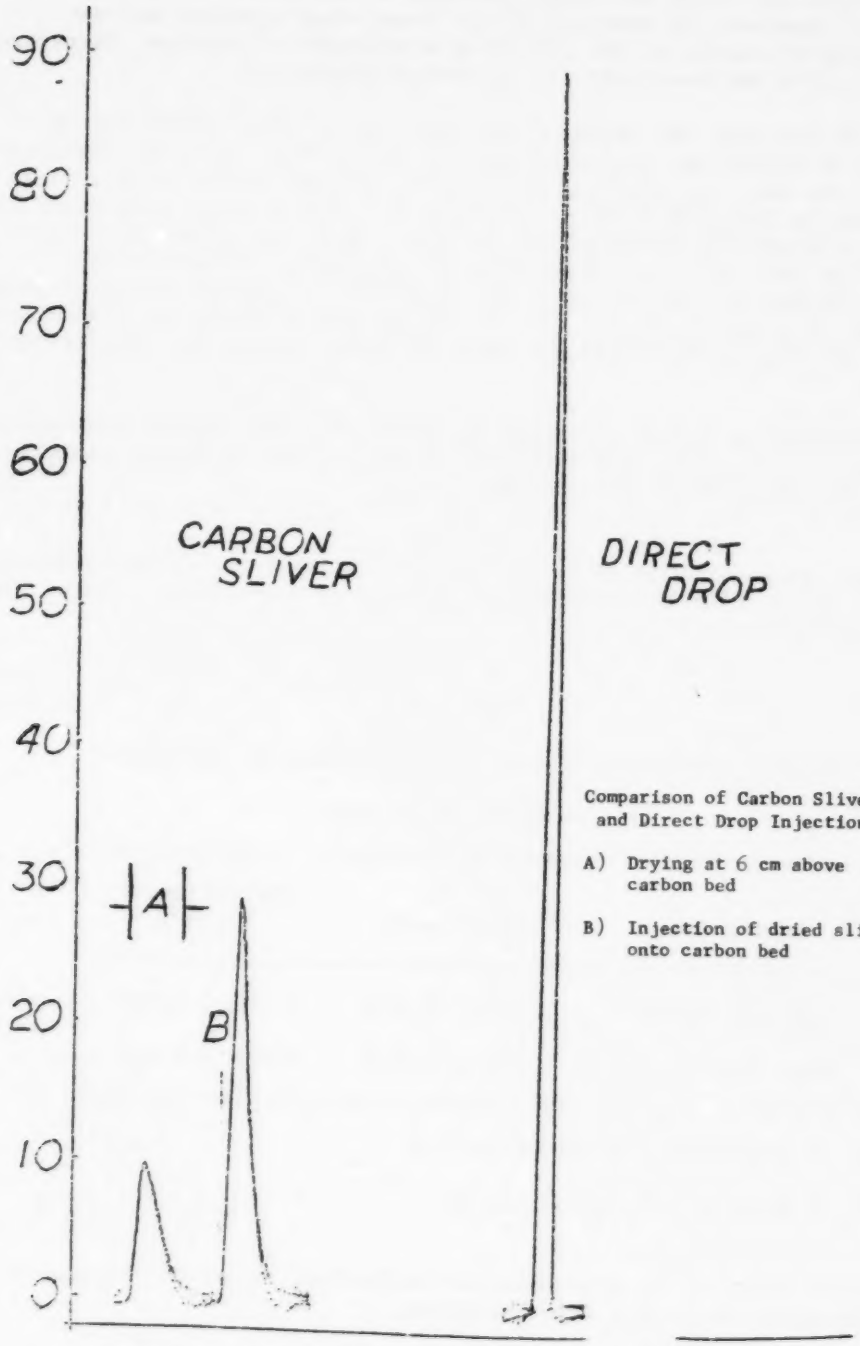


Figure 17. Absorption Traces Cd Introduced on Carbon

Conclusions. It was felt that this technique was successful in providing a method for the direct determination of cadmium in the atmosphere in real time. There appeared to be no complications in the technique and it was felt that the ease in the determination of cadmium indicated the wide applicability of this method to metals in air analysis.

SECTION IX

DETERMINATION OF ARSENIC

Arsenic was chosen as the next element to study for several reasons. First, it is known to be highly toxic and a dangerous air pollutant. Secondly, the standard techniques for the estimation of arsenic involve scrubbing large volumes of air and analyzing the trapped arsenic by colorimetric methods of analysis or flame atomic absorption spectroscopy.

Arsenic has proven to be one of the more difficult elements to determine by any technique. There are virtually no colorimetric methods which are highly sensitive and with a sufficient degree of selectivity to give reliable quantitative data. Many techniques used are based on the reduction of arsenic to arsine AsH_3, which evolves from the system. The separated arsine is then determined either by atomic absorption spectroscopy or colorimetric analysis. In either case, the end point is difficult to control and the results are always suspect.

For this reason it was decided that arsenic would be a challenging element to study. The development of a reliable rapid method of analysis would be highly desirable.

Detection of Arsenic in the Atmosphere. The system was set up in the normal method using an arsenic hollow cathode and the monochromator was set at 18197 Å, the most sensitive absorption resonance line of arsenic. Air was drawn through the atomizer and the absorption signal measured as previously mentioned. Typical results are shown in Figure 18.

The results were very encouraging and indicated that arsenic in the ambient atmosphere could be detected by this system. It now remained to calibrate the method in order to translate the absorption signal to a concentration of arsenic in the air.

Methods of Calibration. The Direct Drop Technique. A solution of arsenic was made up to contain a 1000 parts per million of arsenic. From this stock solution a number of standard solutions were prepared with concentrations varying from one part per million to a hundred parts per million.

Samples varying from 2 µl to 5 µl were measured accurately using a syringe and dropped directly into the atomizer. Results showed that the absorption signal obtained was highly unreproducible. Even though an absorption signal could be obtained for solutions containing one part

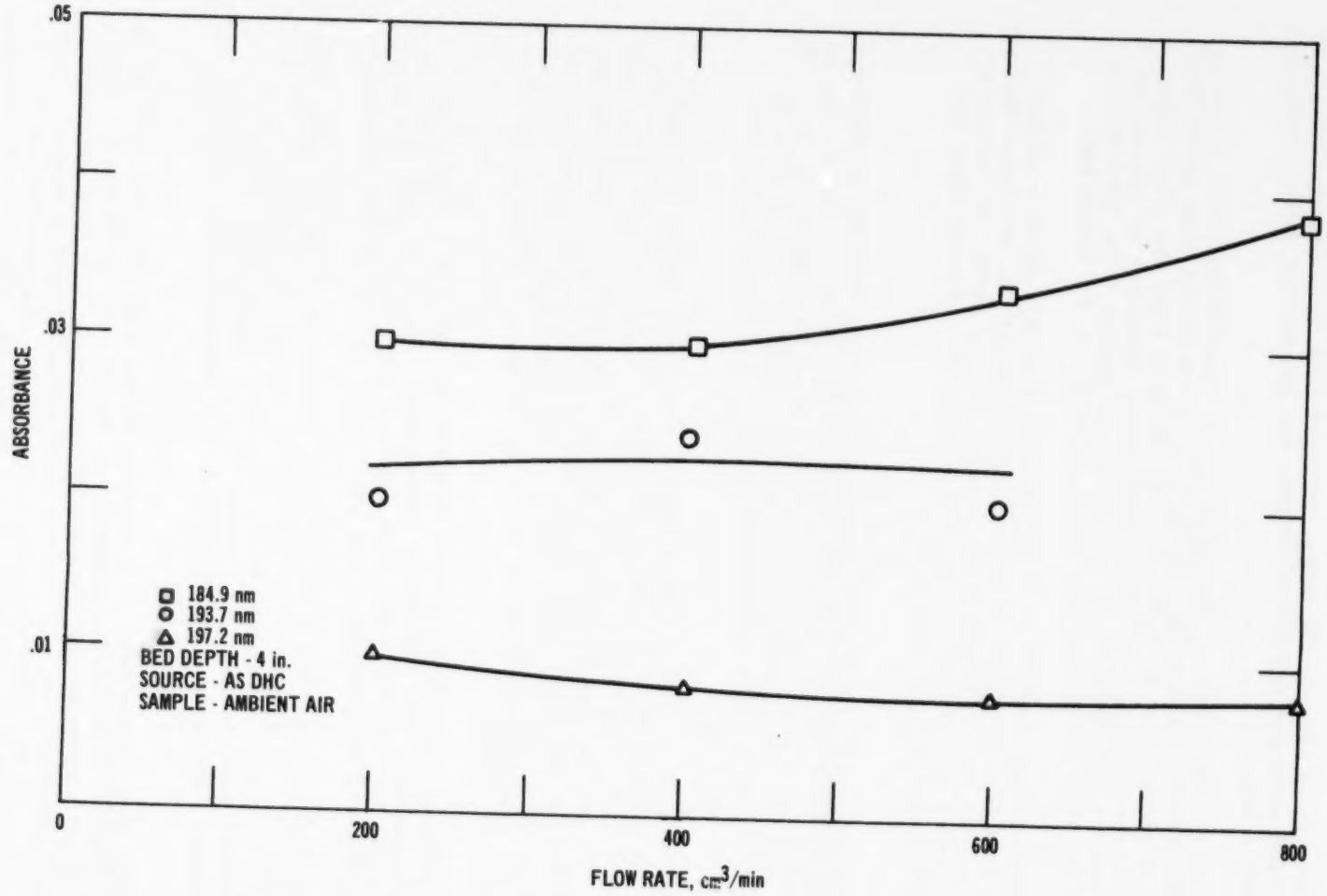


Figure 18. Absorption by as in the ambient air using three different resonance lines.

per million of arsenic the signal obtained from the solutions containing a hundred parts per million of arsenic was greater but did not conform to Beer's Law.

Frequently, there was an absorption signal immediately after injection of the arsenic followed by a second absorption signal some period later. This is illustrated in Figure 19. The delay between the first signal and the second signal was not reproducible. Sometimes it was one or two minutes and sometimes it was up to ten minutes. The data seem to indicate that the arsenic was held up somehow on the carbon bed.

A search of the literature indicated that no stable arsenic carbon compounds had ever been isolated. It was, therefore, concluded that if there was a reaction between the arsenic and the carbon the nature of the product was not known. Similar results were obtained when the platinum wire technique was used.

The Use of Arsine in Calibration Procedures. One possible problem area was that the solutions used were in some way losing the arsenic on the sides of the vessels or that the metal was plating out on the walls of the syringe. Precautions were taken to eliminate this problem by making up calibration solutions freshly (within hours) before all studies were made.

As an extra precaution we investigated the use of arsine as a reagent for calibrating the procedure. The first attempt to do this was made by generating arsine from an acid solution. This proved to be a very inefficient and unreproducible technique. The technique could perhaps have been standarized to provide a reproducible amount of arsine, but considerable time would have been necessary to provide such a procedure. It was, therefore, decided to buy a small cylinder of arsine gas from a commercial source.

It is known that arsine is very sensitive to light and water vapor, particularly if the two are in combination. Therefore, all precautions were taken to prevent light from reaching the arsine and to insure that the compound was protected from water vapor in the ambient atmosphere.

The first approach taken was to flush arsine into a bottle fitted with a rubber cap. A glass syringe was pushed through the rubber cap and a known volume of arsine was extracted. This arsine vapor was then injected directly into the atomizer bed and the absorption signal measured. As before, the signal was very unreproducible.

Atomic Form of Arsenic. A literature survey indicated that arsenic in the gaseous form existed primarily as As_4 at room temperature. This conclusion was based on the experimental observation that the vapor pressure of arsenic in a gaseous state coincides with a molecular weight of As_4. As the temperature was increased the concentration of As increased, and the concentration of As_2 and As_4 progressively decreased.

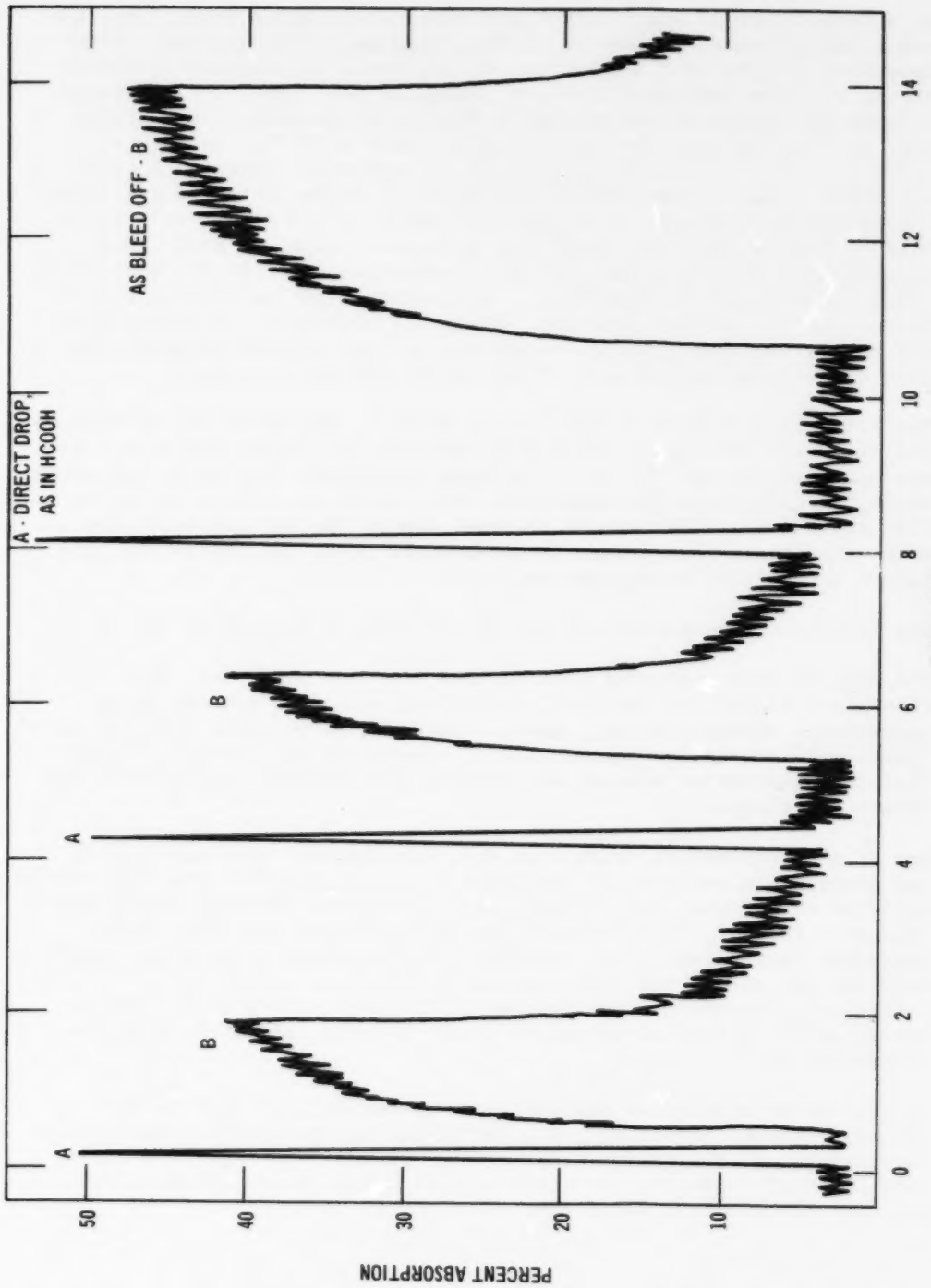


Figure 19. Absorption trace of as indicating delayed signal.

At a temperature of about 1600°C and under equilibrium conditions, the vapor was estimated to consist of As_4, 55%; As_2, 45%; As, 10%. It is important to note that neither As_4 or As_2 would be expected to absorb strongly at the resonance lines of elemental As. Under these circumstances the degree of absorption of freely liberated As would depend very much on the equilibrium conditions under which the arsenic was reduced to free metal. This would be an important variable in flame atomizers. Also it was anticipated that any delay in taking the atomic absorption measurement (as in our instrument) would result in a rapid loss of free As from the system and a rapid decrease in analytical sensitivity. This proposal was tested experimentally on the equipment which was designed in this work. Indications were the arsenic was reduced in the atomizer section. Since the absorption is measured in the absorption tube there was evidently a delay between formation of free arsenic and measurement of the atomic absorption signal.

Two attempts were made to verify this affect. The first was to increase the flow rate and the second was to decrease the carbon bed size. It was proposed that if the flow rate were increased, then more free atoms would be forced into the absorption tube before they could recombine to form As_2 and As_4. The second proposal was if the bed was decreased in size, then again more atomic As atoms would reach the absorption tube before recombining to As_2 and As_4.

The results of the experiment are illustrated in Figures 20 and 21.

The data clearly indicated that as flow rate was increased, the absorption signal did increase, indicating more free arsenic atoms reached the absorption bed. Also, a decrease in bed size resulted in an increase in absorption signal, again, supporting the thesis proposed that the equilibrium between As_2 and As_4 very drastically affected the absorption signal.

One of the conclusions drawn from this experimental work was that if the bed temperature was greatly increased (e.g., to 2500°C), the equilibrium would be thrown over very drastically to cause an increase in As concentration. Further, if the absorption tube was kept at a very much increased temperature, e.g., 2500°C, the percentage of As would remain high and the absorption signal would be increased accordingly. It was determined, therefore, that increasing the temperature of the entire system would be very advantageous in the case of elemental arsenic determination.

At this point studies on arsenic were discontinued because we had already embarked on making a new instrument to operate at a much higher atomization and absorption temperature. It was felt that it would be more fruitful to devote our efforts to building this instrument and evaluate arsenic at a later date.

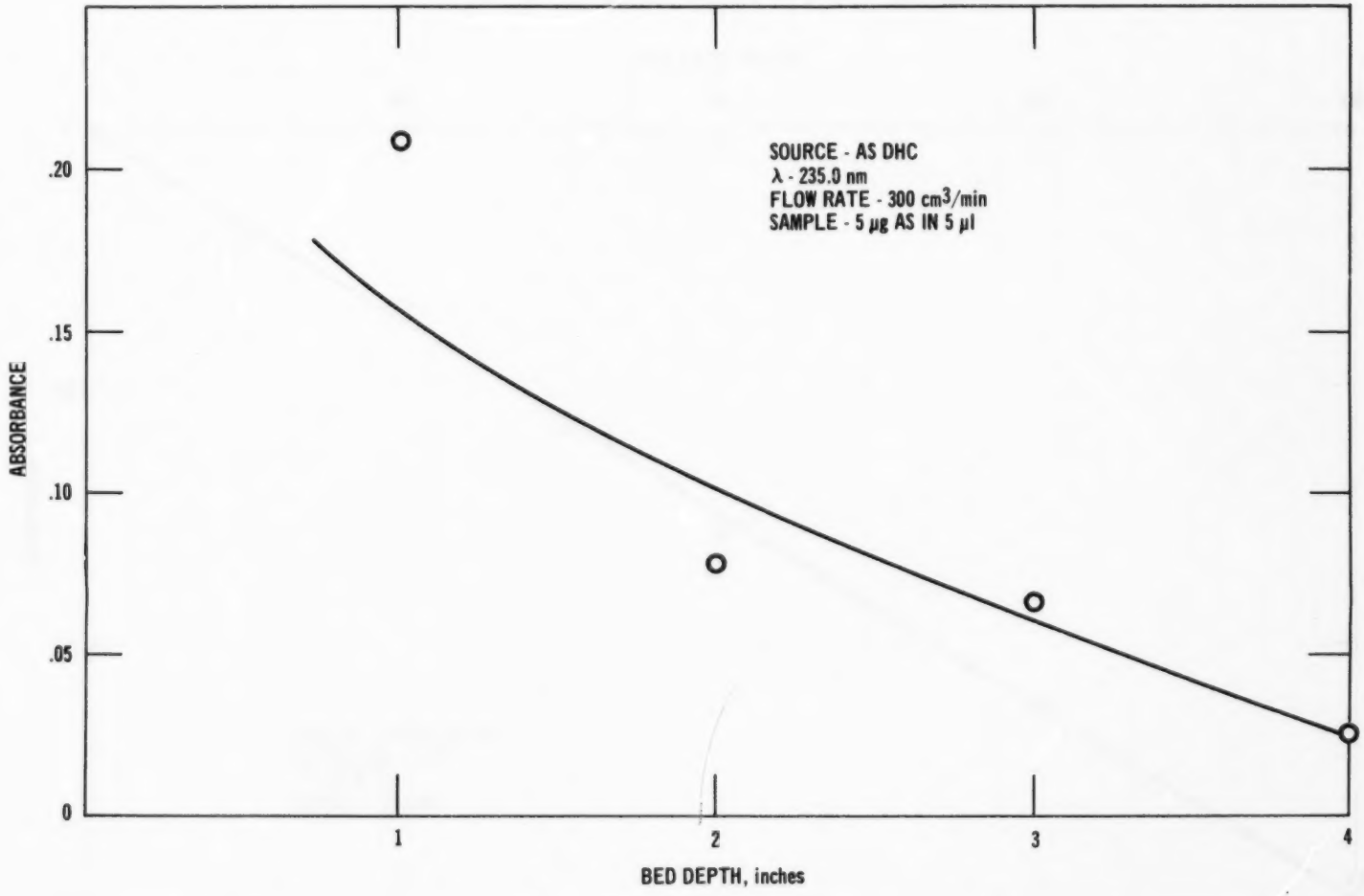


Figure 20. Effect of bed depth on arsenic absorption.

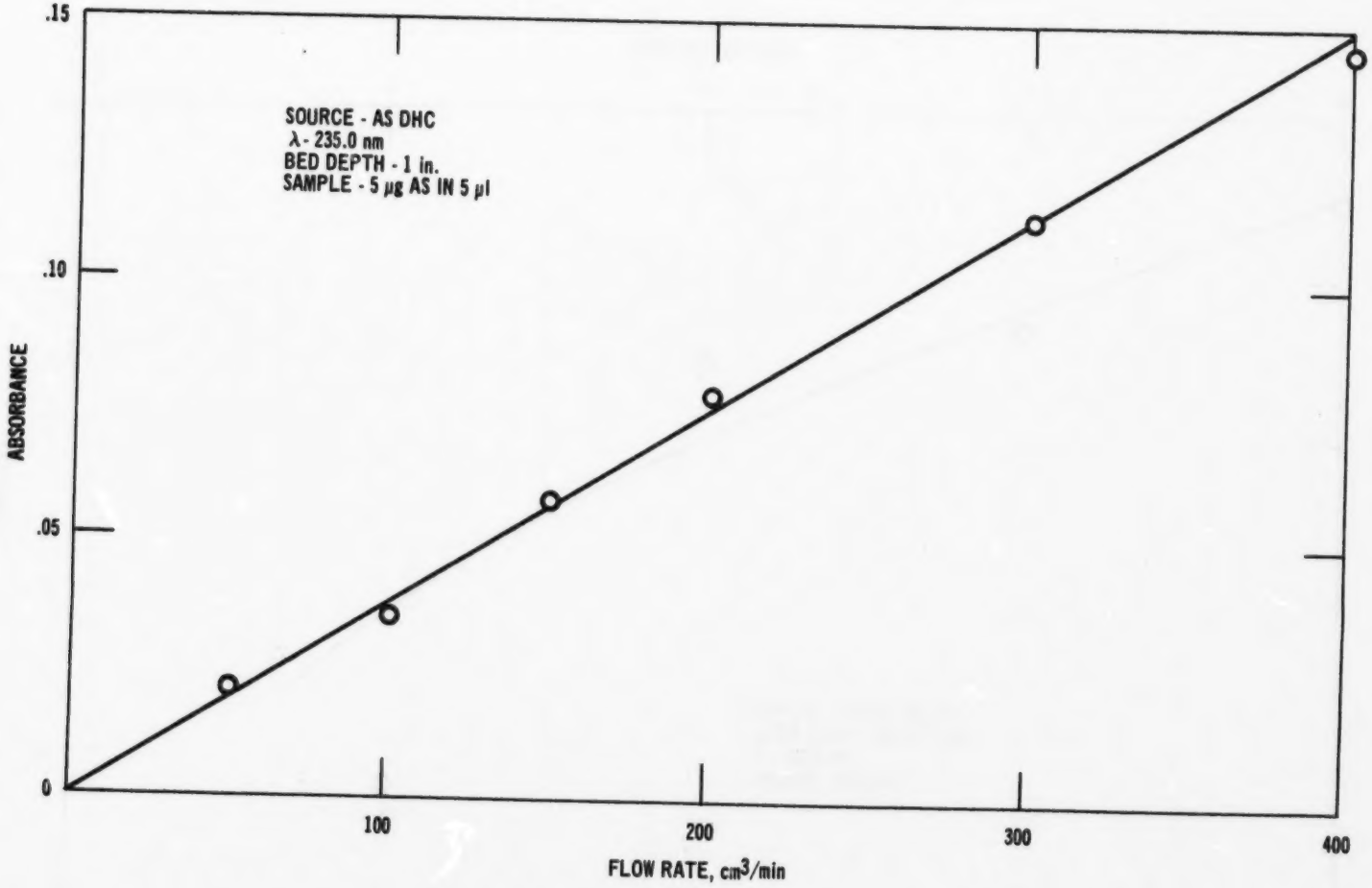


Figure 21. Effect of flow rate on arsenic absorption.

SECTION X

OTHER ELEMENTS STUDIED

Preliminary studies on a number of other elements were carried out. These studies were primarily to get an indication of analytical sensitivity and of problems involved with these elements. The results are outlined below.

Selenium. Selenium is an element similar in many respects to arsenic, both in some of its biological effects and in its chemical properties. It is known to form Se_2 and Se_4 at room temperature, in much the same way as arsenic does.

Preliminary studies showed that selenium was similar to arsenic in its behavior in this instrument. On ocassions, sensitive atomic absorption data were obtained and other times it was difficult to detect the selenium even under fairly high concentrations. In light of our experience with arsenic, it was decided not to pursue our studies with selenium at this point but to delay further studies until the high temperature instrument was completed.

Copper and Zinc. Absorption signals from copper and zinc in the laboratory atmosphere were detected by drawing air through the instrument as described previously.

Typical absorption signals are shown in Figure 6.

The wavelengths used for these measurements were copper, 3248 Å and zinc, 2138 Å.

Attempts to produce calibration curves in order to relate the absorption signals to the quantity of zinc or copper in the atmosphere were unsuccessful. In the great majority of cases, the background signal obtained when the instrument was turned on was 100 percent absorption for each of these elements. This indicated that under the conditions of operation, high concentrations of copper and zinc were reaching the absorption tube. These impurities were probably coming from the carbon rods used to make up the reduction bed. Collaborative studies with both Pocographite and Ultracarbon (pure carbon manufacturers) were carried out. In an effort to eliminate all copper and zinc from the carbon used, each of these companies took special precautions to eliminate all sources of these elements from their manufacturing system. This, of course, included all brass items, copper items or galvanized items.

In addition, each company independently treated the resultant graphite by extended heating at high temperatures (such as 2000°C) for 24 and for 48 hours.

In each case there was little improvement in the background signal obtained for either of these elements. In practice, it would be vital

to be able to clean up the instrument to remove such background. Otherwise, absorption signals from known air samples could not be measured.

The perplexing thing about this study was that occasionally a batch of carbon rods would be obtained which generated very little background and which cleaned up rather quickly when put into the atomizer section and heated up. We were unable to trace the reason for this inconsistency in the manufacturing process and discontinued studies at this time on these two elements.

Another source of possible contamination was the quartz used for making the atomizing system. It is planned to use various types of quartz from different manufacturers to see if this eliminates the problem. It is also anticipated that when we go to a high temperature system, the copper and zinc contaminants will be greatly reduced or eliminated from the system because of the elevated cleansing temperature available.

In a most important previous observation both copper and zinc were detected and measured directly in the atmosphere with reasonanble backgrounds. This illustrated the feasibility of using this instrument for monitoring copper or zinc in the air.

Sodium. Preliminary studies indicated that an absorption signal can be obtained from sodium in the laboratory atmosphere. This illustrated the capability of the instrument for measuring this element directly.

In a similar manner to copper and zinc, a very high background was frequently found when studies on sodium were carried out. It was quite possible that this background came from the quartz used since cadmium is generally at least a minor component in this type of material. It was decided that the high temperature system may solve many of these problems.

Similar observations were made for potassium, i.e., it could be detected in the atmosphere by direct measurements but calibration was difficult because of the high background of potassium.

Iron. This element has a considerably higher boiling point than many of the elements examined hitherto. It was observed that the background signal could be decreased to a reasonable level by heating the bed up to operating temperature for an hour to ninety minutes, during which time purified air was continually drawn through the instrument.

Attempts made to prepare a calibration curve showed that the absorption signal was very erratic for a constant concentration of iron. It was shown that the absorption signal was very sensitive to small changes in temperature of the atomization bed. It was concluded that operating at temperatures around 1400°C in the atomizing bed was too low. Presumably, the temperature is at the critical low end of the permissible temperature for operation of the atomization system.

It was concluded that rather than try to optimize conditions and control conditions rigidly, it would be better to operate at a high temperature system wherein the temperature of the bed would not be critical and reproducible analytical data could be obtained, even with variations in bed temperature. It was concluded, therefore, that the study of iron would be more profitable when the high temperature system was built.

We were unable to detect Be, Mg, Ca or Mg in the air, or when a solution containing 1 μg of the element was introduced into the system. Each of these elements forms refractory oxides which may not be reduced at these temperatures. A higher temperature system was indicated.

SECTION XI

DISCUSSION

Studies Involving the Use of high Temperature Atomizers and Absorption Systems. Based on the results obtained from this project, it is clear that certain elements present as air pollutants can be detected directly without prior separation or concentration from large volumes of air. Calibration procedures have been developed which enable us to calculate the pollution levels from the measured absorption signals. It is, therefore, possible to measure metal pollution levels rapidly and in real time.

The three very important elements lead, mercury and cadmium have all been quantitatively determined in the laboratory atmosphere at Baton Rouge. Other elements such as copper, zinc, arsenic, selenium, sodium, potassium, and silver have been detected in the air but quantitative analyses have not yet been developed for these techniques. Preliminary experiments on less volatile elements such as iron, cobalt, etc., indicate that the temperature of the atomizer is too low for practical quantitative work. The degree of atomization is very sensitive to the temperature of the atomizer and at the temperatures used, i.e., 1350-1500°C, relatively small changes in temperature caused significant changes in the absorption signals obtained.

It appears that the best way to overcome this problem is to increase the atomization chamber temperature significantly, i.e., to an order of 2300°C.

It is our intention at this time to design such an instrument and test it for the less volatile metals. In addition, we will continue to study calibration techniques and miniaturization of the present equipment. It is hoped that based on these results the field instrument capable of being moved easily from one location to another will be developed.

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1. "Recent Advances in Instrumentation in Atomic Absorption," J. W. Robinson and P. J. Slevin, American Laboratory, 10-18 (August 1972).

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SECTION XIV

GLOSSARY OF TERMS, ABBREVIATIONS AND SYMBOLS

g - gram

cc - cubic centimeter

K - absorption coefficient at frequency ν

e - charge on an electron

m - mass of the electron

c - speed of light

f - oscillator strength of the energy transition involved in the absorption

N - number of unexcited or ground state atoms in the light path

rf - radiofrequency

Å - Angstrom

mm - millimeter

W - watt

V - volt

^{o}C - degrees Celcius

T.E.L. - tetraethyl lead

i.e. - id est (that is)

µl - microliter

Pt - platinum

% - percent

µg - microgram

$\mu g/m^3$ - microgram per cubic meter

AA - atomic absorption

σ - standard deviation

e.g. - exempli gratia (for example)

Sensitivity. Where sensitivity limits have been expressed they may be considered as that amount of sample required to give one percent absorption. This is sometimes referred to as absolute sensitivity. A concentrational sensitivity is sometimes used in atomic absorption literature which is defined as the concentration of the sample solution required to give one percent absorption.